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# ABSORPTION OF ATMOSPHERIC SULFUR DIOXIDE BY WATER SOLUTIONS, PROTEIN SOLUTIONS, AND SOILS

Raymond M. Manganelli, et al

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# ABSORPTION OF ATMOSPHERIC SULFUR DIOXIDE BY WATER SOLUTIONS, PROTEIN SOLUTIONS, AND SOILS

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RAYMOND M. MANGANELLI, PRINCIPAL INVESTIGATOR

AND

FRANK PETER TERRAGLIO, RESEARCH ASSISTANT

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DEPARTMENT OF ENVIRONMENTAL SCIENCES

RUTGERS UNIVERSITY, NEW BRUNSWICK, N. J.

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## SUMMARY

A laboratory study was conducted to determine the rate and extent of absorption of atmospheric sulfur dioxide by thin films of water solutions. The adsorption by two types of soil also was measured.

Water solutions were exposed in an environmental test chamber to atmospheric concentrations of sulfur dioxide ranging from 0.5 to 10.0 mg. $SO_2/M^3$. Exposure periods varied up to eight hours.

The overall solubility of sulfur dioxide did not follow the law of partial pressures, but it was found that an exponential equation of the general form $S = KC^a$ could be used to describe the solubility, where "S" is the concentration of sulfite in solution and "C" is the atmospheric concentration of sulfur dioxide. By means of this equation and constants derived from experimental tests, the solubility of sulfur dioxide at an atmospheric concentration of 2.70 mg. $SO_2/M^3$ was found to be 8.7 micrograms/ml. The addition of 50 ppm. of $NaHCO_3$ to the water increased the amount of sulfite found in solution to 32 micrograms/ml. and 130 ppm. $NaHCO_3$ increased the solubility to 40.8 micrograms/ml.

It was found that over 98.5 percent of the $SO_2$ in the dilute solutions tested existed as the bisulfite and the rest was present as un-ionized sulfurous acid. The solubility of the un-ionized sulfurous acid was found to follow the law of partial pressures.

Solutions of albumin, fibrinogen, globulin, and hemoglobin were prepared and exposed to atmospheric sulfur dioxide. The albumin, fibrinogen, and globulin coagulated when the pH of the solution reached their isoelectric points. Bicarbonates and phosphates delayed the coagulation, but once the pH decreased to the isoelectric value, the denaturation took place.

Transformation of hemoglobin occurred as evidenced by a decrease in the absorbance of a solution read at 625 millimicrons.

The reactions noted with protein solutions exposed to atmospheric sulfur dioxide were duplicated with sulfuric acid and did not represent specific chemical reactions of sulfur dioxide with the proteins.

It was found that pH and moisture were significant factors in the adsorption of atmospheric sulfur dioxide by soils. In near dry conditions Lakewood soil (pH 4.0) did not retain any sulfur dioxide when 600 liters containing 7.27 mg. $SO_2/M^3$ was passed through 25 grams of the soil. On the other hand, Nixon soil (pH 5.5) in near dry condition retained 1.13 milligrams of sulfur dioxide from 600 liters of air containing 6.03 mg. $SO_2/M^3$. When the soil moisture was increased to 10 percent, the amount retained increased to 0.57 milligrams for the Lakewood soil and 2.91 milligrams for the Nixon soil.

Effects of pH, soil moisture, and $HCO_3(-)$ concentration are discussed.

## INTRODUCTION

Sulfur dioxide is the most common air pollutant existing throughout the world. In relatively high concentrations, sulfur dioxide is a pungent, suffocating, irritating, colorless gas. The average person can detect 8 mg./$M^3$ by odor and taste. At a sulfur dioxide concentration of 27 mg./$M^3$, throat irritation is severe, and the maximum concentration that can be endured for one hour is about 40 mg./$M^3$. Low concentrations of the gas have been shown to be injurious to plants, and to contribute in part to the corrosion of buildings and metal objects. The presence of sulfur dioxide in the air can be shown to lead to the production of aerosols which reduce visibility.

Sources of sulfur dioxide are many and varied throughout a metropolitan community. The gas results from the combustion of coal, fuel oil, natural gas, gasoline, and allied products. Incineration of domestic refuse contributes additional sulfur dioxide to the atmosphere. Other sources of atmospheric sulfur dioxide are the metallurgical industry, food and kindred products, chemical industry, ceramic industry, and the production of pulp and paper.

These sources of sulfur dioxide emit millions of tons of the gas to the atmosphere yearly, yet the concentrations of the gas on a world-wide basis are not continually increasing. The most extensive surfaces with which airborne sulfur dioxide comes in contact are the sea and the soil.

Absorption of sulfur dioxide by water surfaces, whether the sea, surface waters, rain water, or fog has been mentioned as one of the principle removal mechanisms that take place. Reactions with the soil represent another possible removal process.

One of the most important effects of sulfur dioxide is its influence on human health. If the gas reaches the lung, transport to the blood is relatively easy and rapid. Even before reaching the lung the possibility exists of reactions with the mucous lining of the respiratory tract. All cells and tissues of the body are bathed in various type fluids, and before the gas comes into contact with the tissue it first must dissolve in a biological liquid. The rate at which solution of the gas takes place and the amount of sulfur dioxide that is dissolved must be known before any evaluation on health effects can be made.

A study was undertaken to obtain information about the solubility of the gas in water at concentrations near those found in the atmosphere, to determine the extent of adsorption by soils, and to investigate the effect of sulfur dioxide on proteins in solution.

## LITERATURE REVIEW

### A. General

The history of sulfur dioxide as an air pollutant is lengthy and interesting. Some of the earliest writings report of the sulfur oxides that accompanied the burning of coal. While these effects were noted very early, it was at the time of the Industrial Revolution, with its increased fuel consumption, that sulfur dioxide became a general atmospheric pollutant.

The gas arises from the combustion of sulfur compounds which occur in fuel, refining of metal ore, and chemical and petrochemical processes. Additional oxides of sulfur are produced from the incineration of domestic and municipal wastes. Table I lists the sulfur content of various fuels as given by Faith (22). Not all of the sulfur in fuel and waste materials is emitted as sulfur oxides. The total sulfur content of coal consists of three fractions: pyrites, organic sulfur compounds, and sulfates. The sulfates, being in an oxided state, do not contribute to atmospheric sulfur dioxide levels.

The rate at which sulfur dioxide is emitted per unit of material burned, as given by Chambers (14), is presented in Table II. Although the unit emissions of sulfur dioxide appear to be low, the total quantity of the gas released by multiple sources of a metropolis is great. Rupp (62) estimated the yearly sulfur oxide emissions in the United States to be 19 x $10^6$ tons as $SO_2$, and Carey (13) estimated the total for England and Wales to be 4 x $10^6$ tons.

The concentrations of sulfur dioxide in the atmosphere of many cities in the United States are shown in Table III from a report by Wohlers and Bell (79) and the annual report of the New York City Department of Air Pollution Control (19). Inspection of the table shows that only in a few cities does the concentration exceed 1 mg./$M^3$ and then only for short periods of time.

The average values listed in Table III represent, in most cases, the mean value for an entire year. The sulfur dioxide concentrations, however, do not remain constant throughout the year but undergo a seasonal variation as shown in Figure 1. The average monthly sulfur dioxide readings for New York City for 1954, taken from Greenburg and Jacobs (35), showed maximum levels of sulfur dioxide during the winter months when additional fuel is consumed for home heating and for increased power demands.

While the sulfur dioxide concentrations show seasonal variations, daily fluctuations also occur, which are illustrated in Figure 2 from data presented by Greenburg and Jacobs (35). The occurrence of two peaks, one at 0600 to 1000 hours and the other at 1800 to 2200 hours, is a characteristic of the daily variation that takes place in New York City.

## TABLE I

## SULFUR CONTENT OF SELECTED FUELS

| Fuel | Sulfur |
|---|---|
| | wt. % |
| Bituminous coal | 0.3 -5.0 |
| Anthracite coal | 0.7 |
| Most crude petroleum | 0 -1.0 |
| Gasoline, 1951 regular | 0.01 -0.4 |
| Heavy fuel oil | 0.3 -3 |
| Natural gas | 0 -0.03 |
| Manufactured gas | 0.004 -0.04 |

## TABLE II

## SULFUR DIOXIDE EMISSION PER UNIT OF MATERIAL BURNED

| Process | Oxides of Sulfur (as $SO_2$) Emitted |
|---|---|
| Fuel oil combustion | 30 lbs./1000 lbs. of oil |
| Coal burning | 40 lbs./2000 lbs. of coal |
| Automobile engines | 17 lbs./1000 gal. of gasoline |
| Diesel engines | 15 lbs./1000 gal. of fuel |
| Combustion of refuse | 2-8 lbs./2000 lbs. of material |

## TABLE III

## SULFUR DIOXIDE LEVELS REPORTED IN VARIOUS COMMUNITIES (19,79)

| Community | Year | mg. $SO_2/M^3$ | |
|---|---|---|---|
| | | Ave. | Max. |
| Akron, Ohio | 1955 | 0.240 | 0.586 |
| Baltimore, Md. | 1950 | 0.197 | 1.25 |
| Detroit, Mich. | 1955 | 0.080 | 0.346 |
| Donora, Pa. | 1949 | - | 1.86 |
| New York, N. Y. | 1957 | 0.532 | 3.724 |
| | 1960 | 0.478 | 3.192 |
| | 1962 | 0.505 | 3.458 |
| Philadelphia, Pa. | 1955 | 0.239 | 0.586 |
| Washington, D. C. | 1955 | 0.239 | 0.930 |

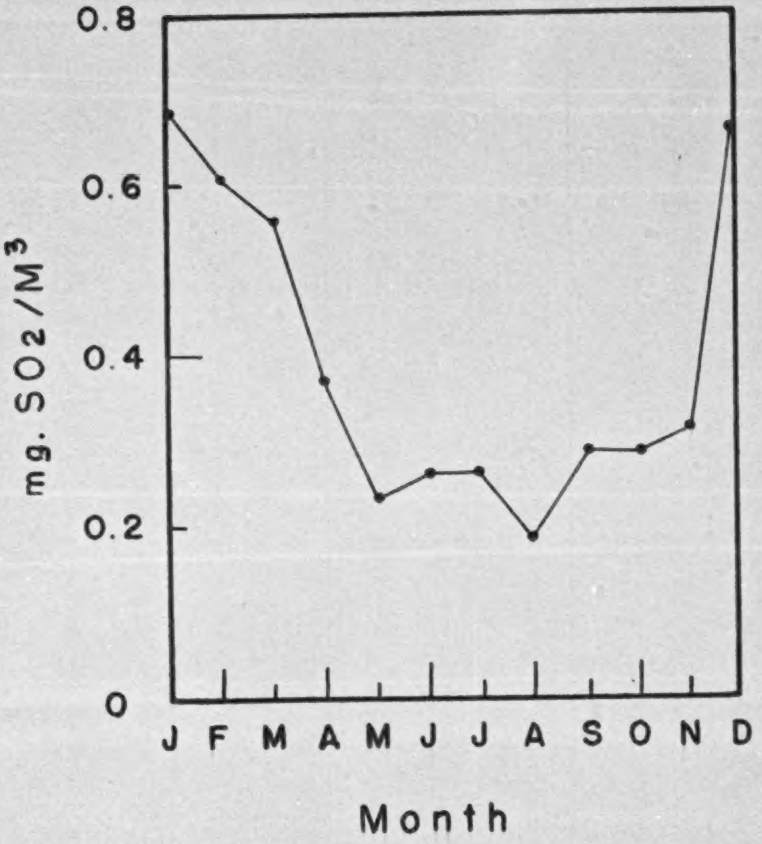

FIGURE 1 - SEASONAL VARIATION OF SULFUR DIOXIDE CONCENTRATION IN NEW YORK CITY -1954

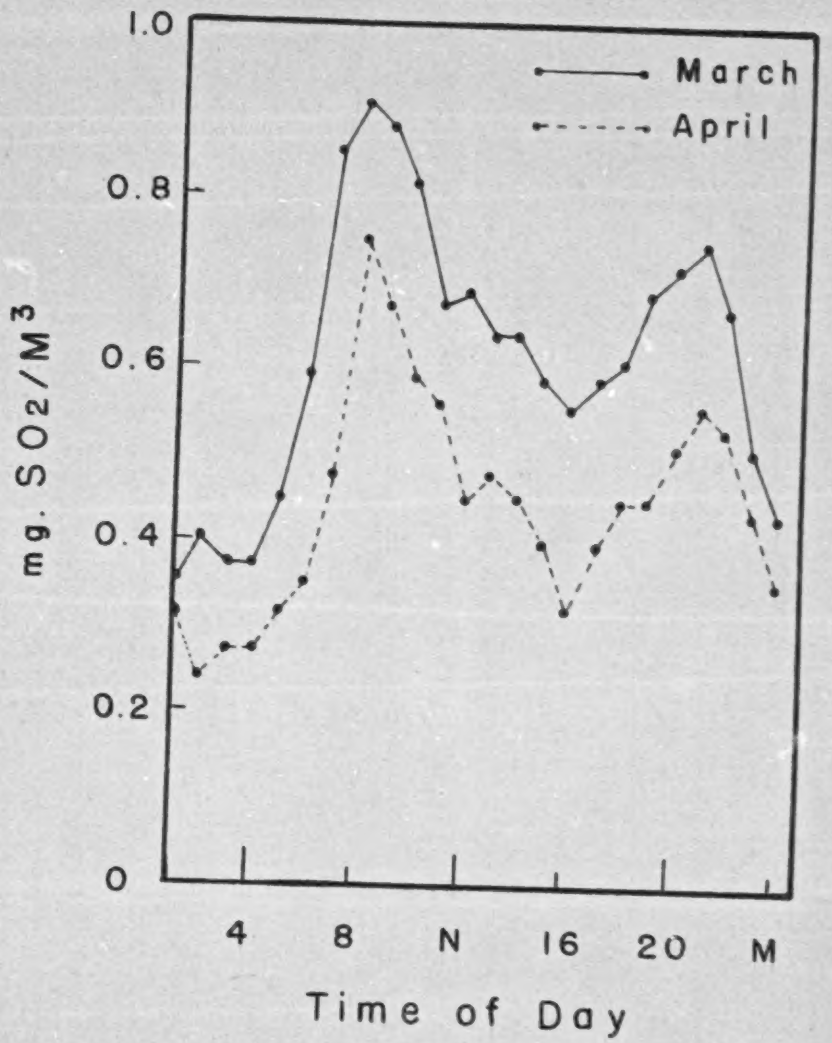

FIGURE 2 - DAILY VARIATION OF SULFUR DIOXIDE CONCENTRATION

IN NEW YORK CITY - 1954

It should be pointed out that individual results that diverge widely from this idealized average pattern can be found at any time of the day and at any time of the year.

The presence of sulfur dioxide in the air is not confined to metropolitan areas but is truly global in distribution. Lodge, MacDonald, and Vihman (52) found concentrations of the gas in the Mid-Pacific as high as 0.122 mg./$M^3$. They also found that even over the ocean 42 percent of the samples they collected contained more than 0.0003 mg. $SO_2/M^3$.

A number of investigators have attempted to work out a world-wide sulfur balance in the atmosphere. Jensen and Nakai (42) have indicated that sulfur dioxide from domestic activity is the prime source of sulfate sulfur in the atmosphere near large industrial and metropolitan centers. Junge (46) has estimated that the industrial sulfur emissions increase the global atmospheric sulfur by 30 percent and, therefore, it is truly a global problem. Junge and Werby (48) have indicated that no sulfur dioxide is emitted directly from the soil but hydrogen sulfide from biological origin is converted in the air to sulfur dioxide and then to sulfate. Estimations of the average residence time of atmospheric sulfur dioxide have been given by several investigators and values are shown in Table IV.

## B. Effects

Human Health and Comfort.--The effects of sulfur dioxide on man and his environment have received a great deal of attention. Heimann (38) has indicated that sulfur dioxide alone or in combination with other atmospheric contaminants was one of the causative agents in the air pollution episodes of the Meuse Valley in 1930, Donora, Pa., in 1948, and London in 1952. In all three of these incidents the primary effect noted was irritation of the respiratory trace. Goldsmith and Breslow (32), Smith (71), and Mallette (53) have stressed the need for further study of the potential hazard to man of airborne chemical irritants.

Elkins (21) has stated that sulfur dioxide being only slightly soluble in the respiratory fluids passes through to a greater extent to the lung and damages it, while Barach (7) has stated that the greatest damage inflicted by sulfur dioxide is to the bronchi. Amdur, Melvin, and Drinker (3) found decreased tidal volume and increased respiratory and pulse rates in human volunteers exposed for 10 minutes to concentrations of 2.66 to 21.78 mg. $SO_2/M^3$. Meetham (54) reported that 100 factory workers exposed only during working hours to 7.98 mg. $SO_2/M^3$ had increased incidence of respiratory infection, abnormal urinary acidity, and shortness of breath.

Dalhamn (17) found no lasting effect in ciliary activity of rabbits exposed for one to two months to 26.6 mg. $SO_2/M^3$. Balchum, Dybicki, and Meneely (5, 6) exposed dogs to radioactive sulfur dioxide in concentrations ranging from 4.78 to 393.7 mg./$M^3$ and found tagged sulfur in every tissue assayed, including blood, eyes and brain. Elfimova and Shashkov (20) reported that breathing sulfur dioxide contaminated air increased the blood concentration of sulfur dioxide.

TABLE IV

AVERAGE RESIDENCE TIME OF SULFUR DIOXIDE IN THE AIR ESTIMATED BY DIFFERENT AUTHORS

| Time | Basis of Estimate | Reference |
|---|---|---|
| 21 - 42 days | Calculated from photochemical oxidation | Gerhard (30) |
| 5 days | Calculated from catalytic oxidation | Junge (46) |
| 12 hours | Estimated from atmospheric measurement | Meetham (54) |
| 3 - 4 hours | Atmospheric sampling | Gartrell, Thomas, and Carpenter (29) |

Amdur (2) found that the presence of sulfuric acid aerosol increased the respiratory response of guinea pigs to sulfur dioxide by an amount greater than could be accounted for by simple addition of the two compounds. She found that even inert aerosols such as sodium chloride increased the response of guinea pigs to all concentrations of sulfur dioxide. It was concluded from her findings that the gas was absorbed on the particles, carried to the lungs, and there set up local areas of high concentration. Gordieyff (33), and Pattle and Burgess (59), however, report that the effect of sulfur dioxide in the presence of inert dusts is not increased by an amount greater than that which could be accounted for by the sum of the effects of the gas and the dusts taken separately.

Much research has been conducted on the secondary effects of sulfur dioxide such as irritation or annoyance due to the reaction products of sulfur dioxide and other materials in the air. Schuck, Doyle, and Endow (66), and Prager, Stephans, and Scott (61) found that sulfur dioxide in the presence of some hydrocarbons, and oxides of nitrogen reacted photochemically forming aerosols that increased light scattering and decreased visibility. Gerhard (30) reported that the photochemical oxidation of sulfur dioxide to sulfur trioxide proceeded at a rate of 0.68 percent per hour in simulated sunlight but only at 0.1 to 0.2 percent per hour with intense natural sunlight. Johnston and dev Jain (43) found that sulfur dioxide reacts with hydrocarbons under the influence of ultraviolet light to form a slow-settling aerosol. Faith, Renzetti, and Rogers (23) report that the solution of sulfur dioxide into water droplets of fogs brings about rapid oxidation of the sulfur dioxide to form sulfuric acid, particularly if metals like iron, manganese, and vanadium are present in the droplet.

Field studies have been undertaken to determine the extent of the conversion of sulfur dixoide to sulfuric acid under natural conditions. Thomas (74) reported that with proper conditions in the atmosphere in Los Angeles, 5 to 20 percent of the total sulfur in the air was present as sulfuric acid. Cholak et al. (15) found more than 90 percent of the sulfurous material in the air over Cincinnati was sulfur dioxide. Katz (49) reported that 82 to 87 percent of the sulfur components in a smoke plume was sulfur dioxide. The intense interest in the form of atmospheric sulfur is based on the fact that sulfuric acid has a more severe physiological effect on man, while sulfur dioxide has a more damaging effect on vegetation.

Vegetation.--Thomas, Hendricks, and Hill (75), and Setterstrom (67, 68) have reported that many environmental conditions such as light, soil moisture, temperature, and soil nutrients, as well as the concentration of sulfur dioxide are important factors in the effect of the gas on vegetation.

Corrosion.--The major factors in the atmospheric corrosion of steel are recognized to be moisture, temperature and sulfur dioxide. Sanyal and Bhadwar (64) found that a specific humidity, the corrosion rate of metals in the presence of 0.3 percent sulfur dioxide is greatly accelerated. The exact humidity at which this acceleration took place varied with each metal and was a characteristic of the metal. They referred to the humidity at which the corrosion rate increased as the critical humidity. Aziz and Godard (4) showed that sulfur dioxide itself was not the controlling factor in the rate of reaction with metals but it is a promoting factor in that corrosion increased if sulfur dioxide was present. They postulated that corrosion was due to absorption of sulfur dioxide in water, oxidation to sulfuric acid, and then reaction of the acid with the metal. Bowen and Gropp (10), however, reported that the corrosion rate of iron in a sulfur dioxide solution was proportional to the sulfur dioxide concentration.

Other materials beside metals are susceptible to attack by sulfur dioxide. Burdick and Barkley (11) in their excellent review of the literature report that cement, limestone, and leather are subject to deterioration by sulfur dioxide. Paper exposed for 10 days to concentrations of sulfur dioxide ranging from 5.32 to 26.6 mg./$M^3$ showed embrittlement. Hudson and Milner (40) used tagged sulfur dioxide to demonstrate both general and localized take-up of sulfur dioxide by paper.

Several theories have been proposed for the mechanism of attack on materials by sulfur dioxide. Katz (50) has postulated that sulfur dioxide is absorbed by water surfaces, and in this form reacts with metals, ceramics, textiles, and paper. Larson (51) has implicated particulate material in acid gas attacks on materials, in that particles retain moisture at the point of contact between the particle and the surface of the material even at low relative humidities. The absorption of pollutants, sulfur dioxide included, provides a site of contact and attack. Yocom (80) brings up another mechanism in the deterioration of materials with the natural cooling that takes place at night causing a condensation of surface moisture on the material. In the presence of corrosive pollutants this surface moisture provides an ideal environment for solution of gas and then corrosive attack.

## C. Solubility

Laboratory studies.--One of the early reports on the solubility of sulfur dioxide was by Sims (70) who found that at pressures of 0.25 atmospheres and below 40°C. the solubility in water was much greater than that predicted by the law of partial pressures. Sherwood (69) extended these findings down to partial pressures (or concentrations) of 1729 mg./$M^3$ of sulfur dioxide and found the solubility to be 0.2 g. $SO_2$/1000 g. of water at 20°C. Johnstone and Leppla (45) reported the solubility of sulfur dioxide in water as 0.16 g. $SO_2$/1000 g. of water when the atmospheric concentration was 700 mg./$M^3$. Johnstone and Coughanowr (49) determined the rate of absorption of sulfur dioxide at atmospheric concentrations of 53.2 to 532 mg./$M^3$ in drops containing catalysts and found that the solubility was a function of the concentration of sulfur dioxide and the nature of the catalyst. Junge and Ryan (47) reported that the sulfur dioxide dissolved in water droplets was not oxidized in the absence of a catalyst. Many studies (8) on the solubility of sulfur dioxide in water deal with the removal of the gas from attack emissions were it is present, generally, in concentrations above one percent.

Field Studies.--Junge (46) reported that sulfur dioxide removal is achieved predominantly by precipitation. The removal process is solution in fog droplets, catalytic oxidation by metals in the droplet, and finally precipitation. Over land the presence of soil dusts with components accelerate the oxidation of sulfur dioxide resulting in high removal of sulfate and increasing the sulfate content of rivers to values much higher than can be accounted for by the weathering of rock and soil. Meetham (54) has reported that in London some sulfur dioxide is removed from the air by solution in cloud droplets, falling rain, and in surface waters, but less than one fifth of the sulfur dioxide emitted to the atmosphere is brought down with the rain. A similar quantity escapes by being blown to sea. Much of the remainder is reported as dissolved in the water on buildings, soil, and vegetation, both after rain and at other times. Newall and Eaves (58) found no correlation between rainfall and daily sulfur dioxide concentrations.

pH.--Houghton (39) found the pH of fog and cloud water to be as low as 3.0 in parts of New England, and he ascribed this to the solution of sulfur dioxide and sulfuric acid from the air into the water droplets. Copson (16) reported the pH of rain water samples at Bayonne, New Jersey, have been as low as 4.1.

## D. Soils

The land surface of the earth could be considered a water surface as soil contains varying amounts of moisture depending on environmental conditions. Fortmann (26) stated that sulfur dioxide deposits acidify the soil and require excess amounts of basic fertilizer from outside sources. Junge (46), and Junge and Werby (48) reported that no sulfur dioxide is released directly from the soil.

Sorption of several gases by soil and clay minerals has been reported by Nakayama and Scott (56) who found that variations in sorption were dependent on chemical combinations of gas and components of the soil. They reported that the water content of soil was a large determining factor in sorption of gases and, as the water content increases the amount adsorbed approached the solubility in water. Sameshima and Hemmi (63) measured the sorption of sulfur dioxide by zeolites and bentonites and found the adsorption at one atmosphere pressure for different minerals ranged from 1 to 70 cc/g. of clay with the major portion of the adsorption taking place in the first few hours followed by a slow approach to an equilibrium condition. Fuhr, Bransford, and Silver (28) exposed 13 sq. ft. of soil containing 11 percent moisture to atmospheres containing 5000 to 10,000 mg. $SO_2/M^3$ for one hour. They found that after 40 minutes all of the sulfur dioxide had disappeared. In a control, without soil, 35 percent of the original sulfur dioxide remained after one hour. Alway, Marsh, and Methly (1) exposed samples of surface soil in the field for one month and found adsorption of sulfur dioxide. Bienstock and Field (9) found that many metal oxides adsorbed sulfur dioxide.

## E. Protein Solutions

The lining of the throat is covered with mucous whose chief components are polysaccharides (31). The chief proteins that are present are albumin, fibrinogen, and globulin. These three proteins, as well as hemoglobin, are the most abundant proteins found in the blood.

Elfimova and Shashkov (20) reported that breathing sulfur dioxide contaminated air increased the blood concentration of sulfur dioxide. Balchum, Dybicki, and Meneely (5, 6) used radioactive sulfur dioxide and found tagged sulfur in the lungs, liver, spleen, kidney, and the brain of dogs breathing the gas. They postulated that sulfur dioxide is attached in some manner to the protein of plasma and tissue. Strassi (72) found that exposure of rabbits for a few minutes to 1330 mg. $SO_2/M^3$ caused a decrease in the total protein in the blood. Bystrova (12) reported that the resistance of the mucous membrane of the upper respiratory tract of rabbits exposed to 20 to 200 mg. $SO_2/M^3$ decreased and he found rapid penetration into the blood, followed by a decrease in the hemoglobin content of the blood. Schrenk et al. (65) reported that blood samples from 114 persons living in Donora, Pa., and who had been ill during the smog of 1948 showed no abnormal absorption curves. They concluded that no contaminants were present which would cause blood changes. Grant (34) found that sulfate analysis in the blood must be determined in the alkaline range to prevent binding of sulfur dioxide by the protein. Sulfur dioxide recovery was only 50 to 60 percent in the acid range. Findlay and Williams (25) found that hemoglobin increases the solubility of some gases, sulfur dioxide included, in water and they ascribe this to chemical combination of sulfur dioxide with the protein.

## F. Areas Requiring Study

The complete fate of sulfur dioxide after release to the atmosphere has not been determined. Removal by land and sea surfaces must play an important part in the ultimate fate of the gas. Reactions in the atmosphere, either photochemical or with other suspended matter, have been shown to require moisture before the reactions take place. The action of sulfur dioxide on non-viable material requires solution of the gas, in traces of water at least, before the attack can take place. Before a complete evaluation can be made on the ultimate fate of atmospheric sulfur dioxide, as well as its influence on corrosion and deterioration of materials, information about the solubility of the gas in water, at concentrations near those found in the atmosphere, must be obtained.

Many authors (38, 55, 57, 60, 76) have stressed the need for data relating to the solubility of sulfur dioxide in fluids lining the respiratory tract and in other body fluids. The complexity of most biological fluids makes it difficult to determine the influence of each of the components of the fluid on the solubility of the gas. The exposure of simple water solutions of proteinaceous materials to sulfur dioxide in concentrations ranging from one to ten mg./$M^3$ to determine the solubility of the gas, as well as the effect of the gas on the protein, is required before the entire effect of the gas on living systems can be evaluated.

The information required, therefore, is the rate and extent of solution of atmospheric sulfur dioxide in water and water solutions as well as the influence of moisture on up-take by soils.

# METHODS AND PROCEDURES

## A. Chamber

The absorption and reaction studies were carried out in the laboratory using a dynamic test chamber, having a volume of 5.59 $M^3$. A complete description of the physical construction and operation of the chamber has been given by Terraglio (73). For all of the studies reported the temperature was maintained between 23°C. and 27°C. and the relative humidity ranged from 50 to 80 percent.

## B. Sulfur Dioxide

Preparation of Concentration.--Constant levels of sulfur dioxide were produced in the chamber by preparing cylinder dilutions of sulfur dioxide in nitrogen at a one percent concentration. The diluted sulfur dioxide was mixed at a constant rate with treated laboratory air and introduced into the test chamber. Concentrations in the chamber were monitored by a Davis Electroconductivity meter (18) which recorded the attainment of an equilibrium concentration of sulfur dioxide.

Chamber Concentration.--The sulfur dioxide concentration within the test chamber was measured by a colorimetric method described by West and Gaeke (78). Several samples of the air in the chamber were taken during the period of a test, by collection in fritted glass bubblers operated at 3 cu. dec./min. The length of sampling depended on the concentration within the test chamber. Results of the analyses were averaged to determine the concentration of airborne sulfur dioxide that existed in the chamber.

With the generation system used in this study it was not possible to obtain exact predetermined concentrations of the gas, but by variation in the injection rate of the diluted sulfur dioxide it was possible to cover a range of concentrations. At any single injection rate the concentration could be maintained at a relatively constant level. Table V shows the sulfur dioxide concentrations found in the test chamber at various time intervals for five atmospheric concentrations covering the range to be used in this study. The third column represents the background concentration in the chamber when no sulfur dioxide was introduced to the air stream. The other four columns are the recovered sulfur dioxide at four different rates of addition of the gas and covering the range of atmospheric concentrations to be used in the study.

The variation in the concentration within the test chamber amounted to approximately 10 percent for the four runs where sulfur dioxide was added to the chamber. The average for the lowest concentration used was 0.94 mg. $SO_2/M^3$, and the range of the recovered samples was 0.90 to 0.96 mg. $SO_2/M^3$, while at the highest concentration used the average obtained was 8.29 mg. $SO_2/M^3$ with a range of 7.80 to 8.60 mg. $SO_2/M^3$.

## TABLE V

## SULFUR DIOXIDE CONCENTRATIONS IN THE TEST CHAMBER AT VARIOUS TIME INTERVALS

| Number | Time Collected | Control mg. $SO_2/M^3$ | mg. $SO_2/M^3$ Recovered | | | |
|---|---|---|---|---|---|---|
| 1 | 0 hrs. | 0.01 | 0.90 | 2.76 | 5.70 | 7.81 |
| 2 | 1 | 0.01 | 0.96 | 3.14 | 6.07 | 8.60 |
| 3 | 3 | 0.01 | 0.96 | 2.72 | 6.13 | 8.38 |
| 4 | 5 | 0 | 0.94 | 3.06 | 6.00 | 8.35 |
| Average | | 0.007 | 0.94 | 2.92 | 5.97 | 8.29 |

The sulfur dioxide found in the control sample when no sulfur dioxide was added to the chamber represented the sulfur dioxide in the ambient air that passed into the chamber from the laboratory air. All of the results obtained on the control samples were less than 0.01 mg. $SO_2/M^3$ and were not considered to be of sufficient magnitude to interfere with the studies to be undertaken.

## C. Analytical Procedures

Samples exposed in the chamber were analyzed by either the colorimetric method or by the iodimetric method described by Jacobs (41). Those samples to be analyzed by the colorimetric method were transferred to a sodium tetrachloromercurate solution, the trapping media used in the colorimetric method. The absorbed sulfur dioxide was complexed immediately and could be held for subsequent analysis.

When some of the test solutions were exposed, various interferences, such as turbidity, were present that obviated the use of the colorimetric method. In these cases the iodimetric method was used to estimate the sulfite concentration in solution.

Quite often some preliminary test, for example pH determination, was performed on the sample before it was analyzed for sulfite.

## D. Samples

1. Liquid.--The water solutions tested in this study were distilled water, salt water, sea water, acid lake water, solutions of sodium bicarbonate and potassium phosphate, and solutions of albumin, fibrinogen, globulin, and hemoglobin.

Exactly 20 ml. of test solution was placed in shallow dishes which were put into the test chamber after equilibrium conditions had been reached in the chamber. The samples were placed on a shelf that passed through the chamber and left exposed, in the dark, to the atmospheric sulfur dioxide for different periods of time. The procedure was repeated for several concentrations of airborne sulfur dioxide.

The exposure of shallow layers of solution representing essentially surface films insured rapid approach to equilibrium and uniformity of concentration throughout the entire body of solution.

2. Soils.--A study was undertaken to quantitate the up-take of atmospheric sulfur dioxide by two types of New Jersey soils: the Nixon type and the Lakewood type. The Lakewood soil representing a very acid soil, while the Nixon soil had a more normal acidity for soil in this area. The influence of soil moisture on the adsorption of atmospheric sulfur dioxide was determined.

# RESULTS

## A. Solubility of Sulfur Dioxide in Water Solutions

### 1. Distilled Water

a) Introduction.--The solubility of atmospheric sulfur dioxide in distilled water was determined as water was to be used as the common solvent for all of the exposure studies. Information was required as to the rate and extent of solution of atmospheric sulfur dioxide in distilled water before a study could be made on the effects of other materials in solution.

The procedure for exposure of water samples was to place exactly 20 ml. of distilled water in shallow dishes that were 12 mm. deep and 89 mm. in diameter. This resulted in an area of 62.2 $cm^2$ of distilled water exposed with a depth of 0.32 cm. These samples were placed in the test chamber and exposed to various concentrations of atmospheric sulfur dioxide.

A measure of the dispersion that was obtained with exposed samples was determined from the standard deviation calculated for several concentrations of dissolved sulfur dioxide. For this study eight replicate samples of distilled water were exposed in the test chamber. The same procedure was used for three different concentrations of atmospheric sulfur dioxide. The atmospheric concentrations approximated those to be used in the exposure studies. The standard deviations of the dissolved sulfur dioxide found in the distilled water samples after three hours exposure are as follows:

2.56 ± 0.10 micrograms $SO_2$/ ml. water

5.44 ± 0.22 micrograms $SO_2$/ ml. water

8.27 ± 0.59 micrograms $SO_2$/ ml. water

It can be seen from these studies that the deviations are less than ten percent and actually very close to five percent. Since the deviation is recovered sulfur dioxide was small, only single samples were used for the absorption study.

b) Rate of Solution.--The rate of solution of atmospheric sulfur dioxide in distilled water is shown in Figure 3. The amount of sulfur dioxide found in solution increased at a steadily decreasing rate at all atmospheric concentrations. No further increase in amount was found after two hours exposure which indicated that a saturation or equilibrium condition had been reached.

The solubility of sulfur dioxide at an atmospheric concentration of 0.81 mg. $SO_2/M^3$ was 4.53 micrograms/ml. and this was proportionately greater than the solubility at the atmospheric concentration of 8.73 mg. $SO_2/M^3$ where 16.75 micrograms $SO_2$/ml. was found. An increase in the atmospheric concentration greater than ten time resulted in a less than four times increase in the dissolved sulfur dioxide.

From Figure 3 it can be seen that the approach to the saturation value is more rapid at the higher atmospheric concentrations than at the lower. This is illustrated more clearly in Figure 4 which shows the percent of final saturation value reached in each time increment calculated for each dissolved sulfur dioxide concentration. It can be seen that, although all of the samples reached a saturation value in less than two hours, those samples exposed to higher atmospheric concentrations reached saturation sooner.

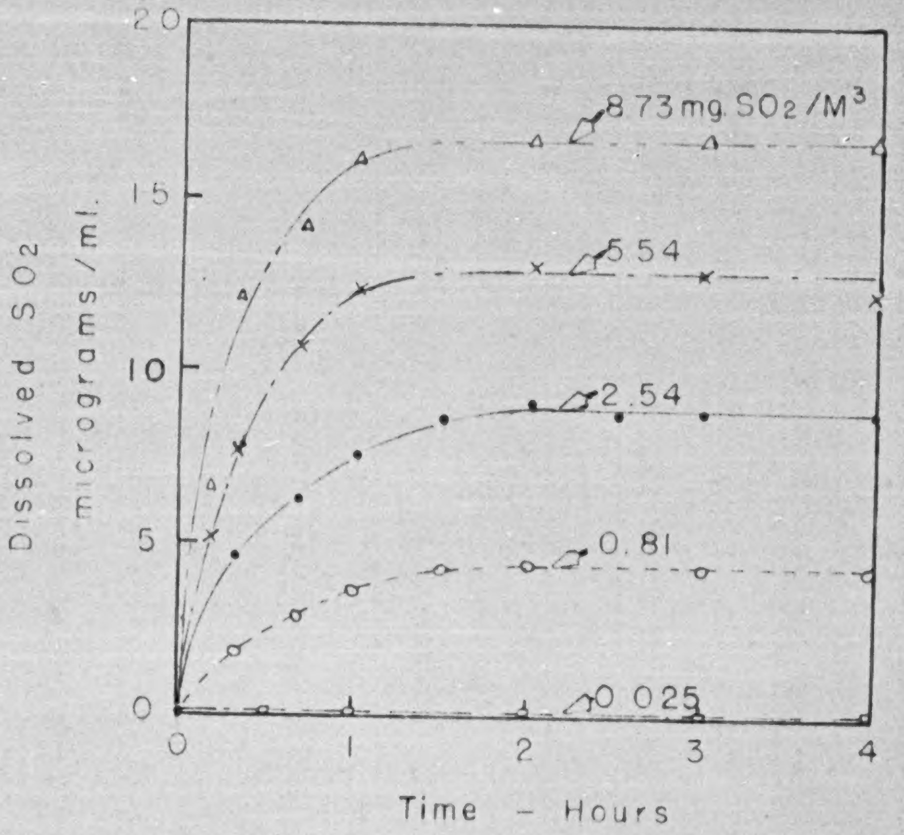

FIGURE 3 - RATE OF SOLUTION OF SULFUR DIOXIDE IN DISTILLED WATER

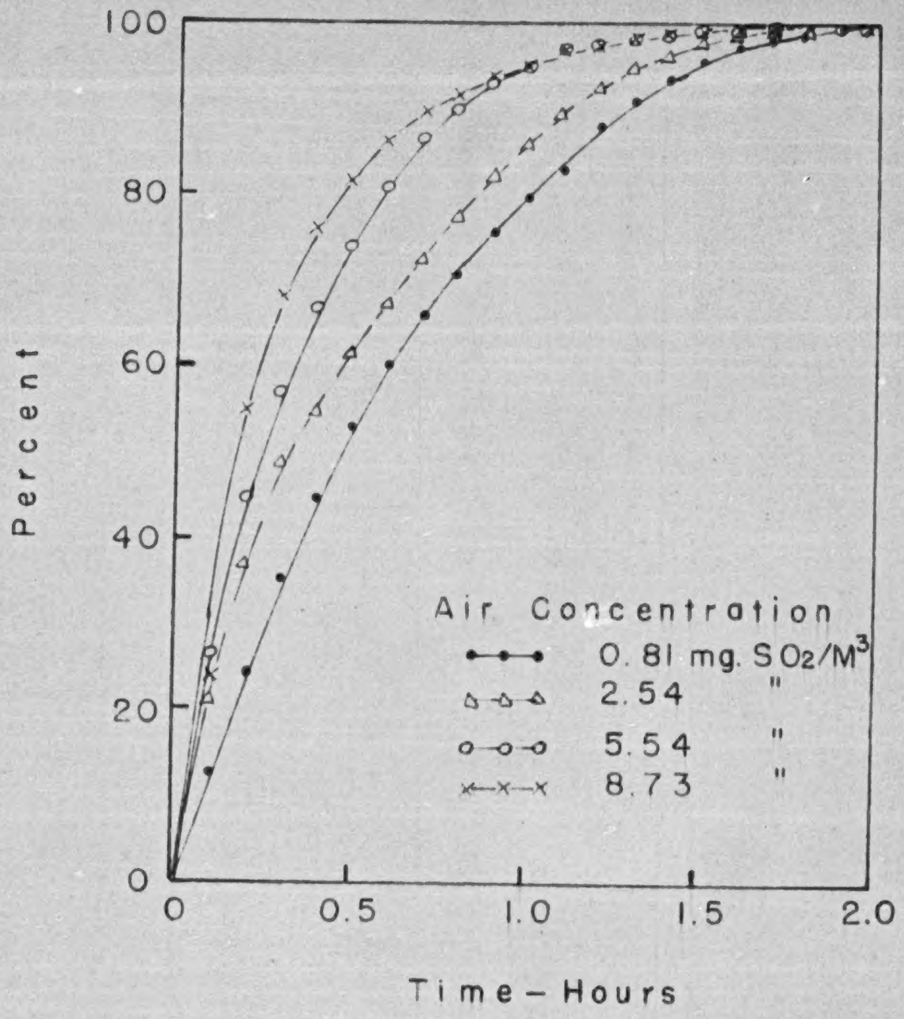

FIGURE 4 - RATE OF SOLUTION OF SULFUR DIOXIDE IN DISTILLED WATER AS PERCENT OF FINAL SATURATION VALUE

While the general shape of the curve suggested a first order reaction, a single rate constant did not describe the solution of gaseous sulfur dioxide in distilled water. The rate constants for the solution of sulfur dioxide in distilled water were as follows:

| Atmospheric Concentration (mg. $SO_2/M^3$) | $k_s$ |
|---|---|
| 0.81 | 0.0060 |
| 2.54 | 0.0140 |
| 5.54 | 0.0209 |
| 8.73 | 0.0231 |

The constants represent the fraction of the unsaturation satisfied in each minute. If the solution of atmospheric sulfur dioxide followed a first order reaction then the constants would have been the same regardless of the concentration. Therefore, the atmospheric concentration of sulfur dioxide is not the only factor influencing the rate of solution of the gas in distilled water.

It was observed that the pH values of the water samples decreased rapidly upon exposure to atmospheric sulfur dioxide and the rate of solution of the gas decreased with the decrease in the pH value. An example is given in Figure 5 which shows the pH of the distilled water samples exposed to 5.54 mg. $SO_2/M^3$.

The rate of solution of the gas was rapid during the first one half hour when the pH value decreased from 6.1 to near 4.0. As the pH of the solution approached 4.0 the rate of solution of atmospheric sulfur dioxide decreased markedly and stopped completely when the pH reached 3.8.

All of the distilled water solutions showed the same pattern of rate of solution changes with decrease in the pH value, except that solution of the gas ceased at slightly lower pH values with the higher atmospheric concentrations. The pH values at which the solution of atmospheric sulfur dioxide ceased are shown in Table VI.

It can be seen that at all of the atmospheric concentrations tested, the solution of the gas ceased when the pH value decreased to near 4.0. Two of the important factors, therefore, that influence the rate of solution of atmospheric sulfur dioxide are the pH of the solution and the concentration of the gas in the atmosphere.

It should be pointed out that the distilled water samples were exposed essentially as surface films with only slight depth. The rate of solution of atmospheric sulfur dioxide in deeper samples of water cannot be determined from this study.

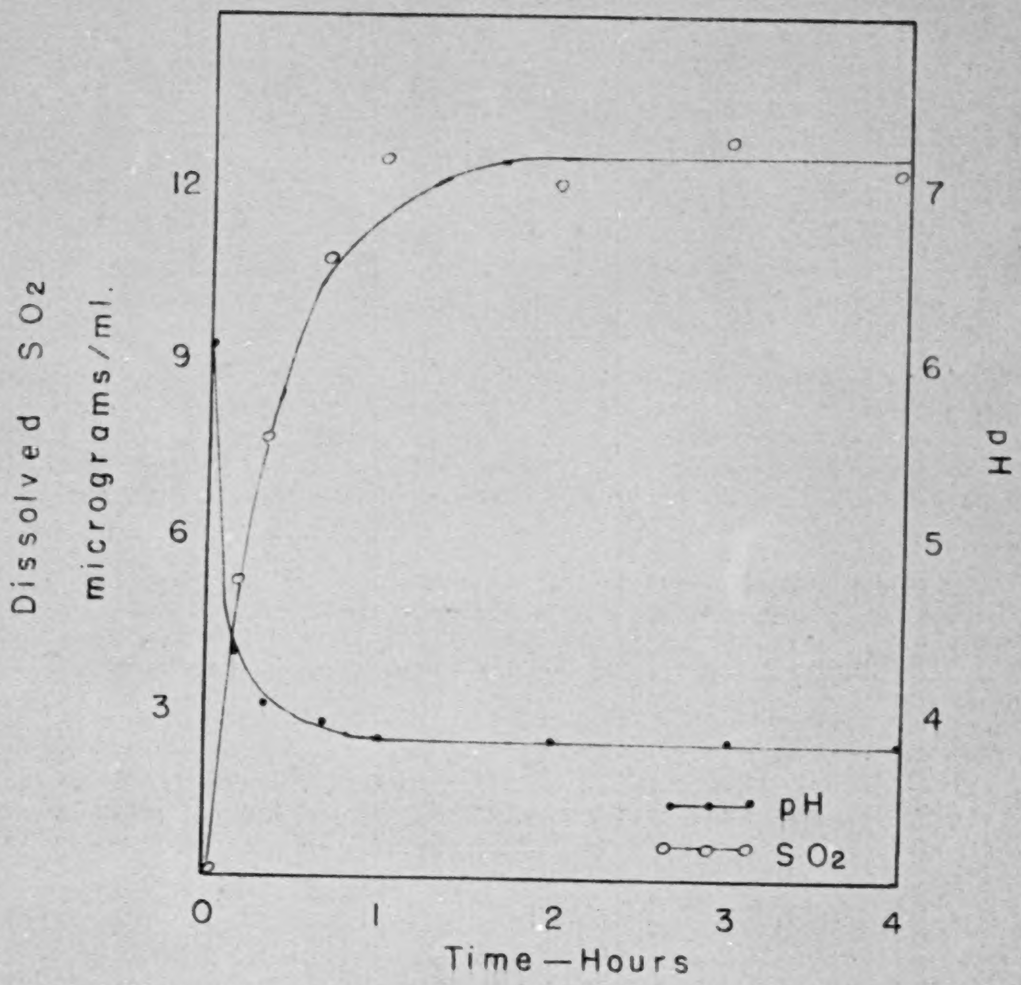

FIGURE 5 - pH OF DISTILLED WATER SAMPLES EXPOSED TO AN ATMOSPHERE CONTAINING 5.54 mg. $SO_2/M^3$

## TABLE VI

## pH OF DISTILLED WATER SAMPLES EXPOSED FOR FOUR HOURS TO ATMOSPHERIC SULFUR DIOXIDE

| Atmospheric Concentration (mg. $SO_2/M^3$) | Solution Concentration (micrograms $SO_2$/ml.) | pH |
|---|---|---|
| 0.81 | 4.53 | 4.1 |
| 2.54 | 8.88 | 4.0 |
| 5.54 | 12.83 | 3.8 |
| 8.73 | 16.75 | 3.7 |

c) Variation in Solubility with Changes in Depth And Surface Areas.--Two studies were carried out to investigate the influence of depth and area on the solubility values. In one case the area of the distilled water was held constant and the volume varied resulting in a variation in the depth. In the second case the volumes of distilled water exposed were held constant and the area varied.

The procedure for the study was to place different volumes of distilled water into the same size dishes. The water samples were placed in the test chamber, which contained 4.28 mg. $SO_2/M^3$. After exposure for 1.5 hours the amount of dissolved sulfur dioxide was determined in all of the samples (Table VII).

The total amount of sulfur dioxide absorbed was a function of the volume of water used so that more sulfur dioxide was dissolved when larger volumes of water were exposed. It can be seen from the Table that when 25 ml. of water were exposed a total of 225 micrograms of sulfur dioxide were absorbed in 1.5 hours, yet when 60 ml. of water were exposed to the same concentration for the same length of time 420 micrograms of sulfur dioxide were absorbed.

While the total amount of sulfur dioxide dissolved was greater with larger volumes of water, the concentration of the gas in solution decreased with increased volume. Column six shows the concentration of sulfur dioxide found in the distilled water samples that had been exposed for 1.5 hours. It can be seen that the 60 ml. sample had a concentration of 7.0 micrograms of sulfur dioxide per ml., while the samples of less than 30 ml. contained 9.1 micrograms/ml. The distilled water samples that have an area to volume ratio greater than 2, that is depths less than 4.82 mm., showed the same concentration of dissolved sulfur dioxide. Solution diffusion, and turbulence of the air and water were sufficient in the physical set-up used to saturate the entire volume of solution exposed. The deeper samples, those with an area to volume ratio of less than 2, probably take longer to reach saturation. Since 20 ml. was the volume to be used for the absorption studies, Table VII would indicate that no advantage would be gained in the use of larger volumes, and, in fact, it would have the disadvantage of a slower approach to saturation.

In order to illustrate this point a study was carried out on the variation in absorption by different volumes of distilled water. Samples of three different volumes of distilled water, 20, 40 and 60 ml., were exposed in the test chamber for 10, 20, 30 and 60 minutes. The surface area exposed was 62.2 $cm^2$ for all of the samples. The atmospheric concentration in the chamber was maintained at 0.81 mg. $SO_2/M^3$. The quantity of sulfur dioxide recovered in these distilled water samples is presented in Table VIII. It can be seen that the concentration of sulfur dioxide found in the 20 ml. samples was greater than that found in the 40 and 60 ml. samples in all cases from 10 through 60 minutes. It took longer for the deeper samples to reach the same concentration as the shallower ones.

## TABLE VII

### ABSORPTION OF SULFUR DIOXIDE FROM AN ATMOSPHERE CONTAINING 4.28 mg./M$^3$ BY DIFFERENT VOLUMES OF DISTILLED WATER EXPOSED FOR 1.5 HOURS

| Volume (ml.) | Area (cm$^2$) | Depth (mm) | A/V ratio | Total $SO_2$ Absorbed (micrograms) | Micro-grams $SO_2$/ ml. |
|---|---|---|---|---|---|
| 15 | 62.2 | 2.41 | 4.15 | 137 | 9.1 |
| 20 | 62.2 | 3.22 | 3.11 | 182 | 9.1 |
| 25 | 62.2 | 4.02 | 2.49 | 225 | 9.0 |
| 30 | 62.2 | 4.82 | 2.07 | 274 | 9.1 |
| 35 | 62.2 | 5.64 | 1.78 | 307 | 8.8 |
| 40 | 62.2 | 6.44 | 1.30 | 334 | 8.4 |
| 50 | 62.2 | 8.05 | 1.24 | 390 | 7.8 |
| 60 | 62.2 | 9.65 | 1.04 | 420 | 7.0 |

## TABLE VIII

## SOLUBILITY OF SULFUR DIOXIDE IN DIFFERENT VOLUMES OF DISTILLED WATER EXPOSED FOR VARIOUS PERIODS OF TIME TO 0.81 mg. $SO_2/M^3$

| Time (min.) | Volume (ml.) | Area ($cm^2$) | Depth (mm.) | A/V ratio | Total $SO_2$ Absorbed (micrograms) | Micrograms $SO_2$/ml. |
|---|---|---|---|---|---|---|
| 10 | 20 | 62.2 | 3.22 | 3.11 | 25.0 | 1.25 |
| 10 | 20 | 62.2 | 3.22 | 3.11 | 26.4 | 1.32 |
| 10 | 40 | 62.2 | 6.44 | 1.30 | 31.6 | 0.79 |
| 10 | 60 | 62.2 | 9.65 | 1.04 | 33.1 | 0.83 |
| 20 | 20 | 62.2 | 3.22 | 3.11 | 45.2 | 2.26 |
| 20 | 20 | 62.2 | 3.22 | 3.11 | 45.2 | 2.26 |
| 20 | 40 | 62.2 | 6.44 | 1.30 | 49.2 | 1.26 |
| 20 | 60 | 62.2 | 9.65 | 1.04 | 55.8 | 0.93 |
| 30 | 20 | 62.2 | 3.22 | 3.11 | 54.7 | 2.73 |
| 30 | 20 | 62.2 | 3.22 | 3.11 | 56.0 | 2.80 |
| 30 | 40 | 62.2 | 6.44 | 1.30 | 67.3 | 1.66 |
| 30 | 60 | 62.2 | 9.65 | 1.04 | 72.0 | 1.20 |
| 60 | 20 | 62.2 | 3.22 | 3.11 | 76.5 | 3.83 |
| 60 | 20 | 62.2 | 3.22 | 3.11 | 77.5 | 3.87 |
| 60 | 40 | 62.2 | 6.44 | 1.30 | 107.8 | 2.69 |
| 60 | 60 | 62.2 | 9.65 | 1.04 | 123.0 | 2.05 |

A further study on the influence of the surface area was carried out by exposing a constant volume of distilled water spread over different areas. The time of exposure was 1.5 hours and the atmospheric concentration in the test chamber was 4.28 mg. $SO_2/M^3$. Table IX shows the take-up of sulfur dioxide by several volumes of distilled water of varying area, all subjected to the same conditions in the test chamber.

The amount of sulfur dioxide absorbed was nearly constant for each specific volume of distilled water used providing the area to volume ratio was greater than 2. The range of absorbed sulfur dioxide for the samples having area to volume ratios greater than 2 was 9.0 to 9.3 micrograms $SO_2$/ml. The first results for 60, 50, 40 and 35 ml. of water all have ratios less than 2, and depths greater than 5 mm., and the concentration in solution is less than that found in the rest of samples ranging as low as 7.0 micrograms $SO_2$/ml.

It was concluded from the results of these studies that the surface area to volume ratio for the exposure studies had to be greater than 2 in order to reach saturation in the shortest time. Since the study was concerned with reactions in surface films of water, 20 ml. samples that resulted in a depth of 3.22 mm. with an area to volume ratio of 3.11 provided adequate solubility data.

d) Fate of Absorbed Sulfur Dioxide.--A study was conducted on the fate of the sulfur dioxide dissolved in distilled water. Several 20 ml. distilled water samples were exposed for 1.5 hours to an atmosphere containing 6.73 mg. $SO_2/M^3$ and treated as follows:

## TABLE IX

### ABSORPTION OF SULFUR DIOXIDE FROM AN ATMOSPHERE CONTAINING 4.28 mg./M$^3$ BY SEVERAL VOLUMES OF DISTILLED WATER, OF VARYING AREA, WHICH WERE EXPOSED FOR 1.5 HOURS

| Volume (ml.) | Area (cm.$^2$) | Depth (mm.) | A/V ratio | Total $SO_2$ Absorbed (micrograms) | Micro-grams $SO_2$/ ml. |
|---|---|---|---|---|---|
| 60 | 62.2 | 9.65 | 1.04 | 420 | 7.0 |
| 60 | 124.4 | 4.82 | 2.07 | 549 | 9.1 |
| 60 | 186.6 | 3.22 | 3.11 | 554 | 9.2 |
| 60 | 248.8 | 2.41 | 4.15 | 548 | 9.1 |
| 50 | 62.2 | 8.04 | 1.24 | 390 | 7.8 |
| 50 | 124.4 | 4.02 | 2.48 | 466 | 9.3 |
| 40 | 62.2 | 6.44 | 1.55 | 334 | 8.4 |
| 40 | 124.4 | 3.22 | 3.11 | 362 | 9.0 |
| 35 | 62.2 | 5.62 | 1.77 | 308 | 8.8 |
| 35 | 124.4 | 2.81 | 3.55 | 319 | 9.1 |

**Sample**

A. After exposure the sample was transferred to a solution of sodium tetrachloromercurate and analyzed by the colorimetric method.

B. Bromine water was added to the sample in order to oxidize all of the trapped sulfite to sulfate.

C. The sample was allowed to stand for 15 hours, in the dark, open to the general laboratory air and then transferred to a solution of sodium tetrachloromercurate and analyzed by the colorimetric method.

D. The sample was allowed to stand for 15 hours, in the dark, open to the general laboratory air and then bromine water was added to the sample to oxidize all of the trapped sulfite remaining to sulfate.

E. The sample was placed in a large container which had been provided with inlet and outlet ports. Air was drawn through a sodium carbonate filter attached to the inlet port of the container, passed over the sample and through the container and then into a fritted glass bubbler containing sodium tetrachloromercurate solution. Air was drawn through the system for 15 hours.

The results of this study, shown in Table X, indicate that the distilled water absorbed about 280 micrograms of sulfur dioxide during the 1.5 hour exposure to 6.73 mg. $SO_2/M^3$. Recovery by the colorimetric method, Sample A, was 283 micrograms, while recovery by the total sulfate method, Sample B, was 280 micrograms of sulfur dioxide in solution. When the distilled water samples were allowed to stand for 15 hours in the laboratory, only 15 micrograms of the original absorbed sulfur dioxide was recovered as sulfite, as shown by number 3, Sample C. Sample D, in which the total sulfate was measured after 15 hours, showed 163 micrograms of sulfur dioxide. Of the 163 micrograms of sulfur dioxide recovered as sulfate, 15 micrograms were present as sulfite, as indicated by the results for Sample C and the remainder had been oxidized to sulfate.

Analysis of the distilled water sample that had been placed in the special container with air passing over the sample for 15 hours, number 6, Sample E, contained 120 micrograms of sulfur dioxide measured as sulfate. This can be compared to the 163 micrograms of total sulfate that was found in Sample D. The amount of sulfur dioxide that was collected in the bubbler from air passed over the distilled water was only 20 micrograms (number 5, Sample E). The amount of sulfur dioxide evolved from solution plus the amount remaining in solution account for only 68.5 percent of the original 280 micrograms of sulfur dioxide that had been absorbed in the original water samples. It was assumed that the remainder of the sulfur dioxide evolved from the solution and reacted with the surfaces of the container and sampling lines.

## TABLE X

## FATE OF ABSORBED SULFUR DIOXIDE IN DISTILLED WATER SOLUTIONS WHICH HAD BEEN EXPOSED TO 6.73 mg. $SO_2/M^3$

| Number | Sample | Time (hours) | Treatment | Micro-grams $SO_2$/ ml. |
|---|---|---|---|---|
| 1 | A | 0 | Colorimetric Method | 283 |
| 2 | B | 0 | Total Sulfate | 280 |
| 3 | C | 15 | Colorimetric Method | 15 |
| 4 | D | 15 | Total Sulfate | 163 |
| 5 | E | 15 | Collected in Bubbler | 29 |
| 6 | F | 15 | Total sulfate left in distilled water solution from No. 5 | 120 |

## 2. Sodium Chloride Solutions

The influence of salt (NaCl) on the solution of atmospheric sulfur dioxide was determined in order to evaluate the possible removal of the gas from the atmosphere by the extensive surfaces of the sea. Since the sea is the largest of the earth's surfaces and the sea contains a high percentage of salt, it would be of interest to know the extent to which sodium chloride affects the solution of atmospheric sulfur dioxide.

The solubility of atmospheric sulfur dioxide in a three percent sodium chloride solution was determined by the same procedure described for the study on the distilled water solutions. Analysis for dissolved sulfur dioxide in the salt solution was by the colorimetric method.

The rate of solution of atmospheric sulfur dioxide in three percent salt water is shown in Figure 6. All of the salt water samples absorbed sulfur dioxide at a steadily decreasing rate for about two hours at which time the absorption ceased indicating a saturation of the solution with the gas at that particular atmospheric concentration. The amount of sulfur dioxide absorbed was a function of the air concentration with greater amounts absorbed at the higher atmospheric concentrations. It can be seen from Figure 6, however, that proportionately less sulfur dioxide was absorbed at the higher atmospheric concentration than at the lower. As an example, the three percent sodium chloride solution exposed to 0.81 mg. $SO_2/M^3$ dissolved 5.1 micrograms $SO_2$/ ml., while the same salt solution exposed to an atmosphere containing 6.73 mg. $SO_2/M^3$ dissolved 13.73 micrograms $SO_2$/ ml.

The standard deviations of ten replicate samples of three percent salt solutions exposed to different atmospheric concentrations of sulfur dioxide were as follows:

5.07 ± 0.26 micrograms $SO_2$/ml.

8.19 ± 0.69 micrograms $SO_2$/ml.

11.02 ± 0.38 micrograms $SO_2$/ml.

13.81 ± 0.91 micrograms $SO_2$/ml.

These data show that the standard deviation of the measurement of dissolved sulfur dioxide ranged from 3.5 to 8.4 percent. This compares with the standard deviation found in the distilled water samples where the variation was less than ten percent.

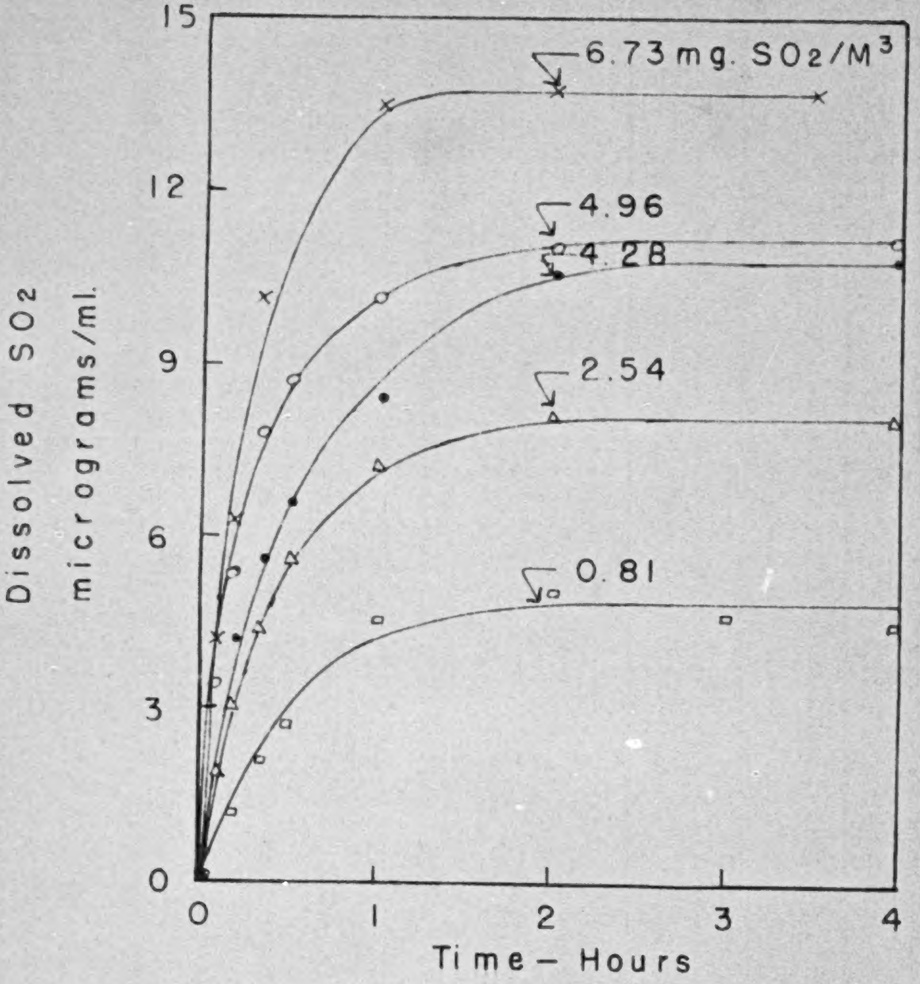

FIGURE 6 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE

IN 3% NaCl SOLUTIONS

The approach to saturation of a salt solution by atmospheric sulfur dioxide was more rapid in general at the higher concentrations than at the lower. This is illustrated more clearly in Figure 7 which shows the percent of final saturation value reached in each time increment calculated for each dissolved sulfur dioxide concentration. It can be seen that the final saturation value for the solution of atmospheric sulfur dioxide in a three percent sodium chloride solution was not reached for over two hours at concentrations ranging from 0.81 to 6.73 mg. $SO_2/M^3$. This can be compared to the solution of airborne sulfur dioxide in distilled water which took less than two hours (Figure 4).

While the general shape of the curve suggested a first order reaction, a single rate constant did not describe the solution of gaseous sulfur dioxide in a three percent sodium chloride solution. The rate constants calculated for the solution of sulfur dioxide in sodium chloride solutions were as follows:

| Atmospheric Concentration (mg. $SO_2/M^3$) | $k_s$ |
|---|---|
| 0.81 | 0.0076 |
| 2.54 | 0.0187 |
| 4.28 | 0.0150 |
| 4.96 | 0.0357 |
| 6.73 | 0.0431 |

The constants represent the fraction of the unsaturation satisfied each minute. If the solution of atmospheric sulfur dioxide followed a first order reaction then the constants would have been the same regardless of the concentration. Therefore, the atmospheric concentration of sulfur dioxide is not the only factor influencing the rate of solution of the gas in a three percent sodium chloride solution.

The solubility of atmospheric sulfur dioxide in a three percent sodium chloride solution exposed for four hours is shown in Figure 8. Also included for purposes of comparison is the solubility of sulfur dioxide in distilled water.

It can be seen that the solubility of atmospheric sulfur dioxide in a three percent sodium chloride solution is only slightly less than that in distilled water, and the difference can be considered insignificant.

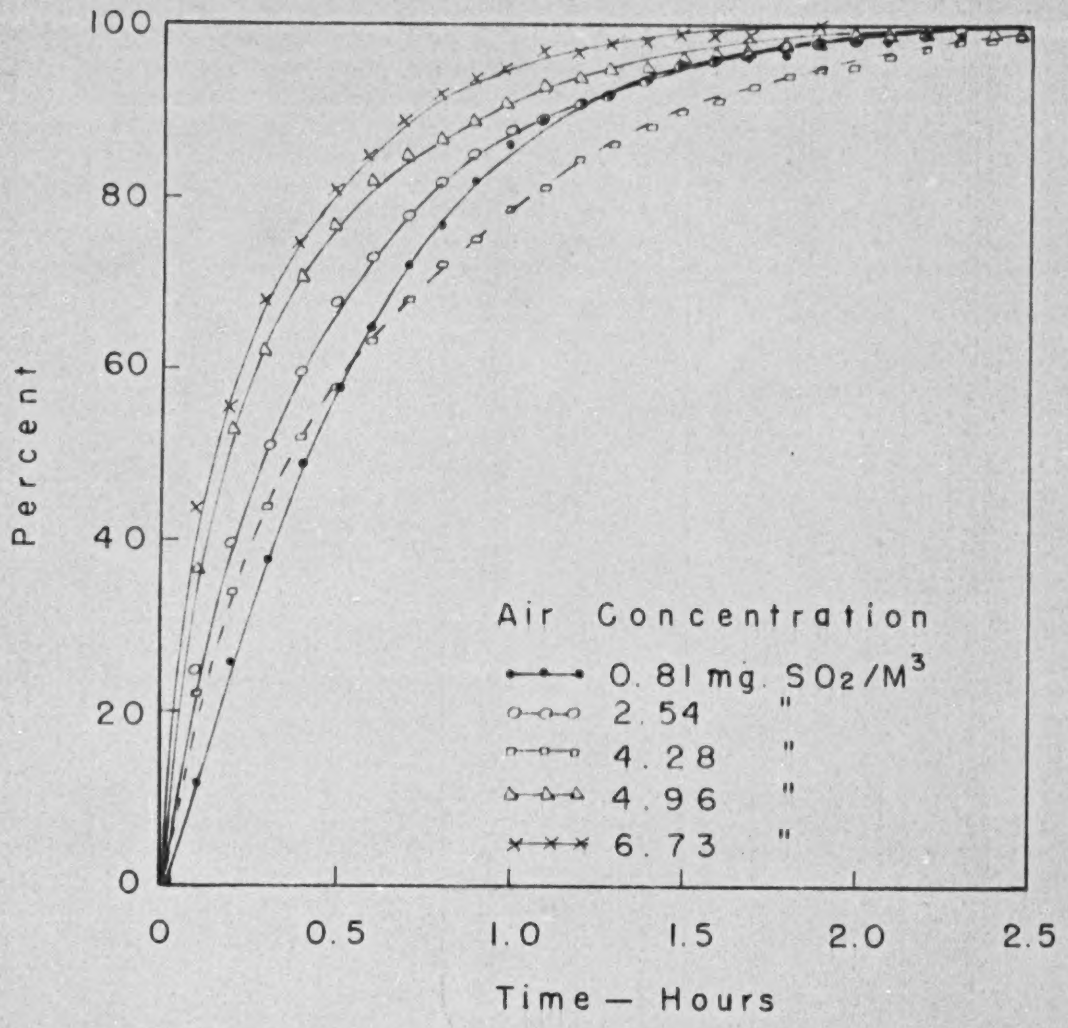

FIGURE 7 - RATE OF SOLUTION OF $SO_2$ IN 3% SODIUM CHLORIDE AS PERCENT OF FINAL SATURATION VALUE

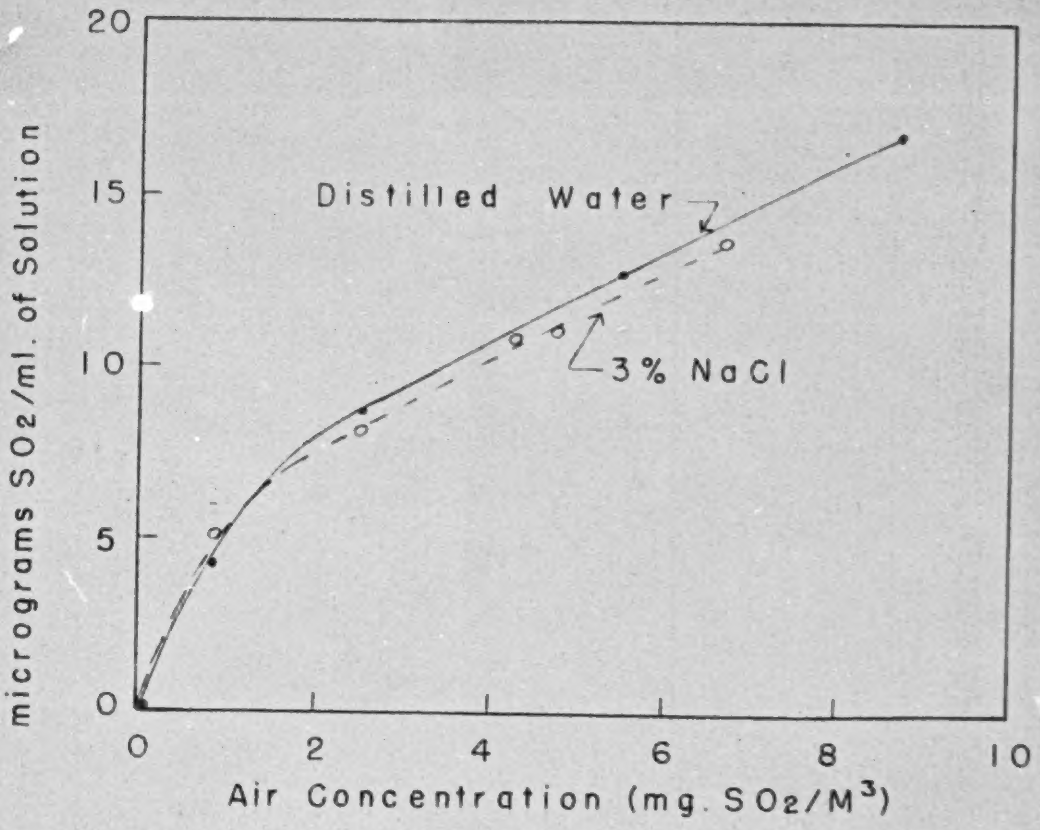

FIGURE 8 - COMPARISON OF SOLUBILITY OF SULFUR DIOXIDE IN FOUR HOUR EXPOSURE OF DISTILLED WATER AND 3% SODIUM CHLORIDE

### 3. Sodium Bicarbonate Solutions

The influence of sodium bicarbonate on the absorption of sulfur dioxide by water was investigated. Distilled water solutions containing 50 and 130 ppm. of sodium bicarbonate were prepared. Samples of the sodium bicarbonate solutions were exposed in the test chamber to atmospheres containing 3.53 and 6.27 mg. $SO_2/M^3$. The rate of solution of sulfur dioxide is shown in Figure 9.

Absorption of the sulfur dioxide by the sodium bicarbonate rose at a steadily decreasing rate and reached a final saturation value that was a function of the concentration of the sodium bicarbonate in solution and of the concentration of sulfur dioxide in the atmosphere. For any specific bicarbonate concentration the amount of sulfur dioxide absorbed was a direct function of the atmospheric concentration of sulfur dioxide. The higher the concentration of sulfur dioxide in the atmosphere the greater was the amount found in solution. For any specific atmospheric sulfur dioxide concentration the greater the amount of sodium bicarbonate in solution the greater the amount of sulfur dioxide absorbed from the atmosphere. The amount of sulfur dioxide dissolved by any specific sodium bicarbonate solution is not a straight line relationship with the atmospheric concentration, as proportionately more sulfur dioxide was found in solutions exposed to lower atmospheric concentrations. The 130 ppm. sodium bicarbonate solution had a final saturation value of 45.0 micrograms $SO_2$/ ml. of solution when exposed to an atmosphere containing 3.53 mg. $SO_2/M^3$, yet when the same solution was exposed to an atmosphere of 6.27 mg. $SO_2/M^3$ the final saturation value was only 64.5 micrograms $SO_2$/ ml.

The absorption by sodium bicarbonate solutions was much greater than that in distilled water or the three percent sodium chloride solutions. The buffer capacity of the bicarbonate in solution permitted greater quantities of sulfur dioxide to go into solution before the pH value decreased to a level that prevented further solution on the gas. Figure 10 shows the change in pH of a 130 ppm. sodium bicarbonate solution that was exposed to an atmosphere containing 6.27 mg. $SO_2/M^3$. The pH value of the solution did not decrease as rapidly as it did in the case of the distilled water samples that had been exposed to the gas as was shown in Figure 5. For a period of approximately one hour the pH decreased very slowly after which it dropped rapidly to a value of 4.5. The change in the pH values of other bicarbonate solutions exposed to the different atmospheric concentrations of sulfur dioxide generally followed the same pattern.

A comparison of the solubility of atmospheric sulfur dioxide in distilled water, three percent sodium chloride solutions and sodium bicarbonate solutions which were exposed for four hours is shown in Figure 17.

## 4. Phosphate Solutions

The influence of phosphate buffer system on the solution of atmospheric sulfur dioxide was studied. Next to the bicarbonate buffer system, the phosphate system is the most important buffer in sea water and its influence on the solubility of airborne sulfur dioxide is important in an evaluation of the fate of emissions of the gas to the atmosphere.

For this study sufficient potassium hydrogen phosphate and potassium dihydrogen phosphate was added to distilled water so that each was $3 \times 10^{-4}M$ in solution. Twenty ml. portions of this solution were exposed in the test chamber to atmospheric concentrations of 3.00 and 6.74 mg. $SO_2/M^3$.

The rate of solution of atmospheric sulfur dioxide in the phosphate buffered solution, Figure 11, is more rapid at the higher atmospheric concentrations. It took less than 1.5 hours to reach the final saturation value in solution when the atmospheric conentration was 6.74 mg. $SO_2/M^3$, while at an atmospheric concentration of 3.00 mg. $SO\ /M^3$ it took approximately two hours to reach the final saturation value?

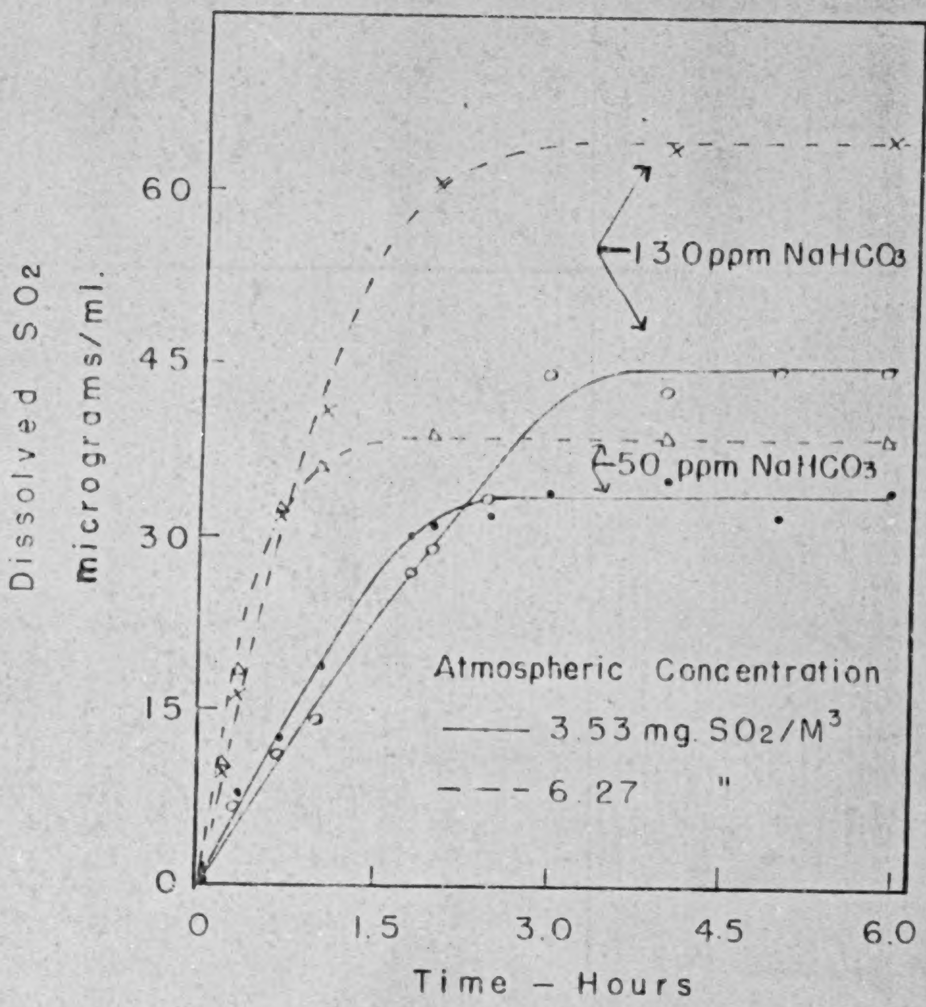

FIGURE 9 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN SODIUM BICARBONATE SOLUTIONS

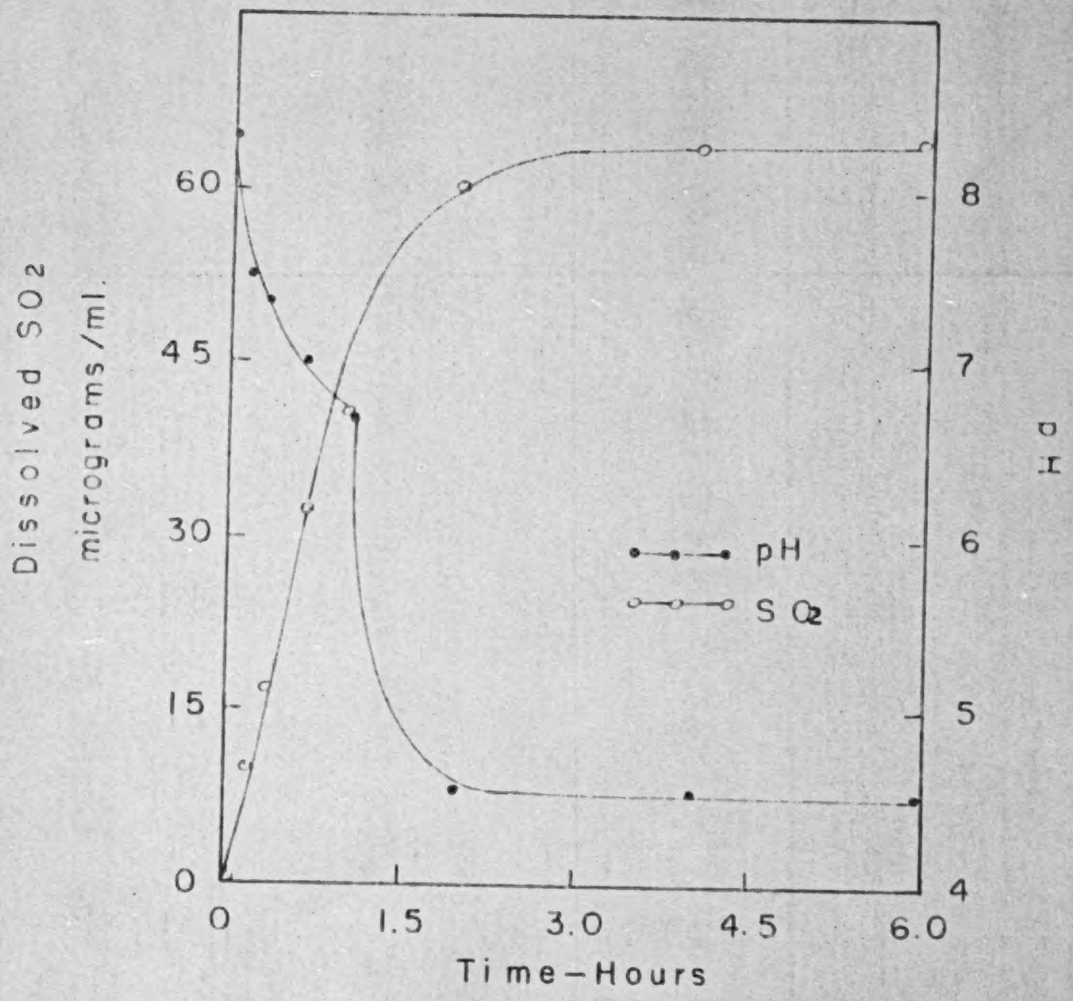

FIGURE 10 - pH OF 130 ppm $NaHCO_3$ SOLUTION EXPOSED TO AN ATMOSPHERE CONTAINING 6.27 mg. $SO_2/M^3$

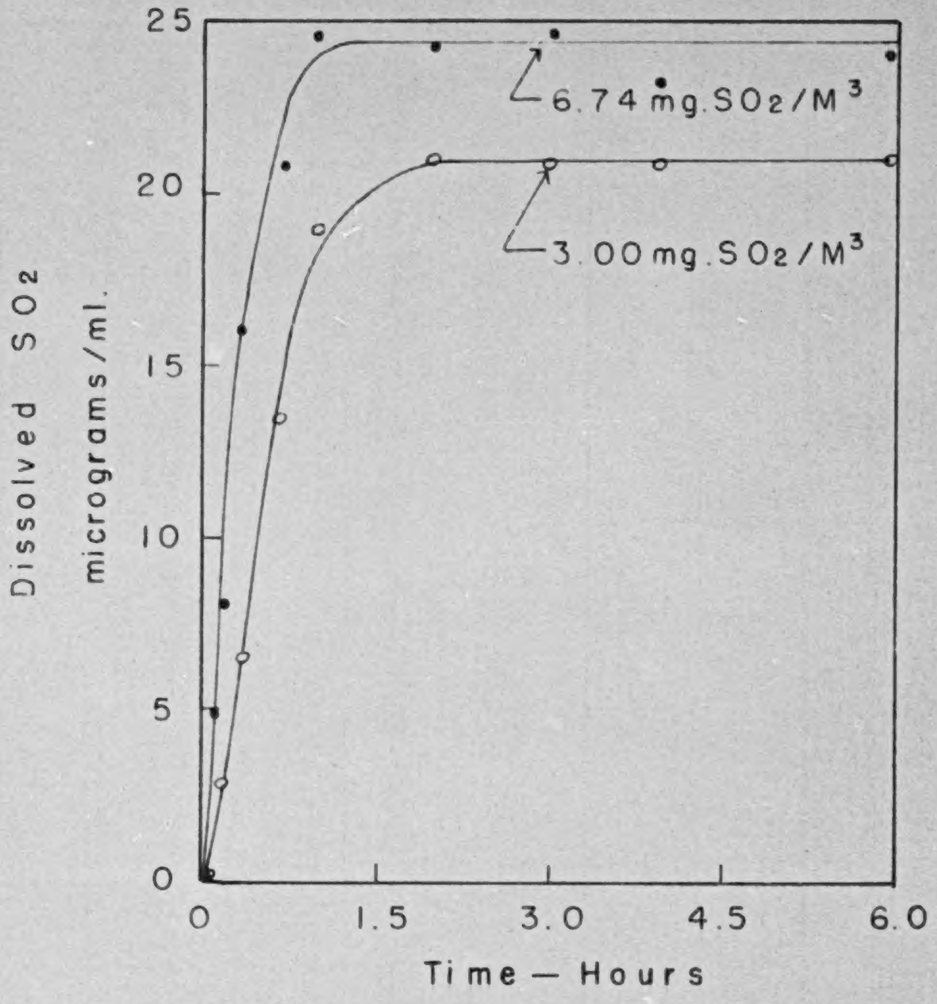

FIGURE 11 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN PHOSPHATE SOLUTIONS

The amount of sulfur dioxide dissolved in the phosphate solution is greater than that which dissolved in the distilled water and three percent sodium chloride solutions, but less than the amounts absorbed by the sodium bicarbonate solutions. The slight increase in the amount of atmospheric sulfur dioxide absorbed by the phosphate solution could be due to the slight buffer capacity that the very dilute phosphate solutions possessed. The pH changes that took place in the phosphate solutions exposed to atmospheric sulfur dioxide, shown in Figure 12, did not exhibit as marked a buffering as did the sodium bicarbonate solutions, but even in this case the drop in pH is not as rapid as that for distilled water as shown in Figure 5. The phosphate served as a buffer to retard pH changes brought about by solution of the atmospheric sulfur dioxide. The rate of solution of the gas remained high until the pH reached a value of 4.5.

### 5. Mixed Solutions

a) Sodium Bicarbonate-Sodium Chloride.--The solubility of atmospheric sulfur dioxide in three percent sodium chloride solutions to which had been added 50 and 130 ppm. sodium bicarbonate was measured. Exposure procedure was to place 20 ml. portions of the mixed solutions in the test chamber for various periods of time. The exposure was repeated for several atmospheric concentrations of the gas.

The rate of solution of sulfur dioxide in the sodium chloride-sodium bicarbonate solutions exposed to atmospheric concentrations of 2.81 and 6.55 mg. $SO_2/M^3$ is presented in Figure 13. Final saturation values for the combined sodium chloride-sodium bicarbonate solutions are lower than the values for sodium bicarbonate solutions and higher than the values for three percent sodium chloride solutions. This is illustrated in Table XI which shows the solubility of atmospheric sulfur dioxide in various sodium chloride and sodium bicarbonate solutions exposed to 2.81 and 6.55 mg. $SO_2/M^3$ for four hours. It can be seen that in general the presence of sodium chloride decreased the solubility of sulfur dioxide in sodium bicarbonate solutions while the presence of sodium bicarbonate increased the solution of sulfur dioxide in three percent sodium chloride solutions.

Figure 13 also shows that the sodium chloride solution with 50 ppm. sodium bicarbonate dissolved more sulfur dioxide than the solution with 130 ppm. of sodium bicarbonate. This finding did not agree with other results presented before where an increase in the sodium bicarbonate resulted in an increase in the amount of sulfur dioxide that was dissolved.

The decrease in the amount of dissolved sulfur dioxide in the sodium chloride solution containing 130 ppm. of sodium bicarbonate after one hour exposure was a drastic variation in the rate of solution. A similar decrease was noted for the solution containing 50 ppm. sodium bicarbonate after one half hour exposure. This was the first instance where an apparent release of dissolved sulfur dioxide took place after it had been trapped in a water solution.

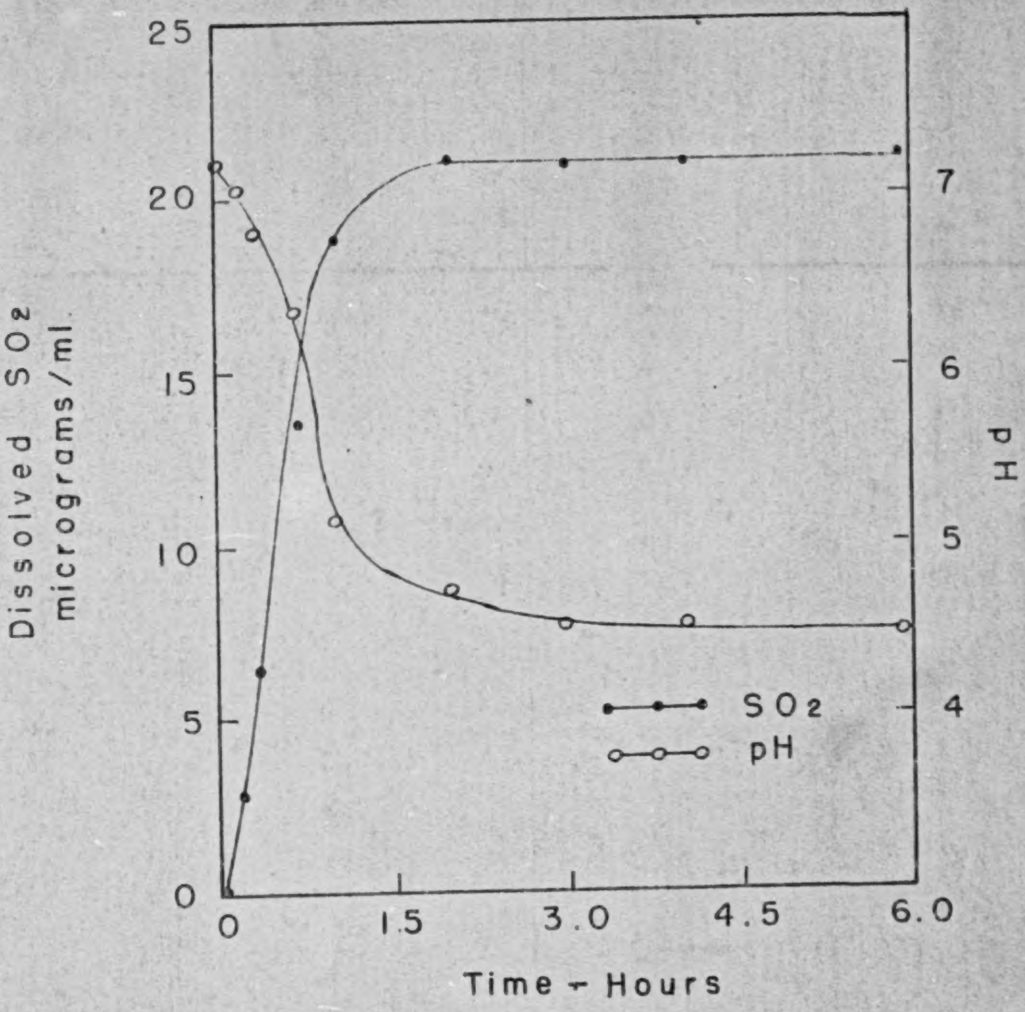

FIGURE 12 - pH OF PHOSPHATE SOLUTION EXPOSED TO AN ATMOSPHERE OF 3.00 mg. $SO_2/M^3$

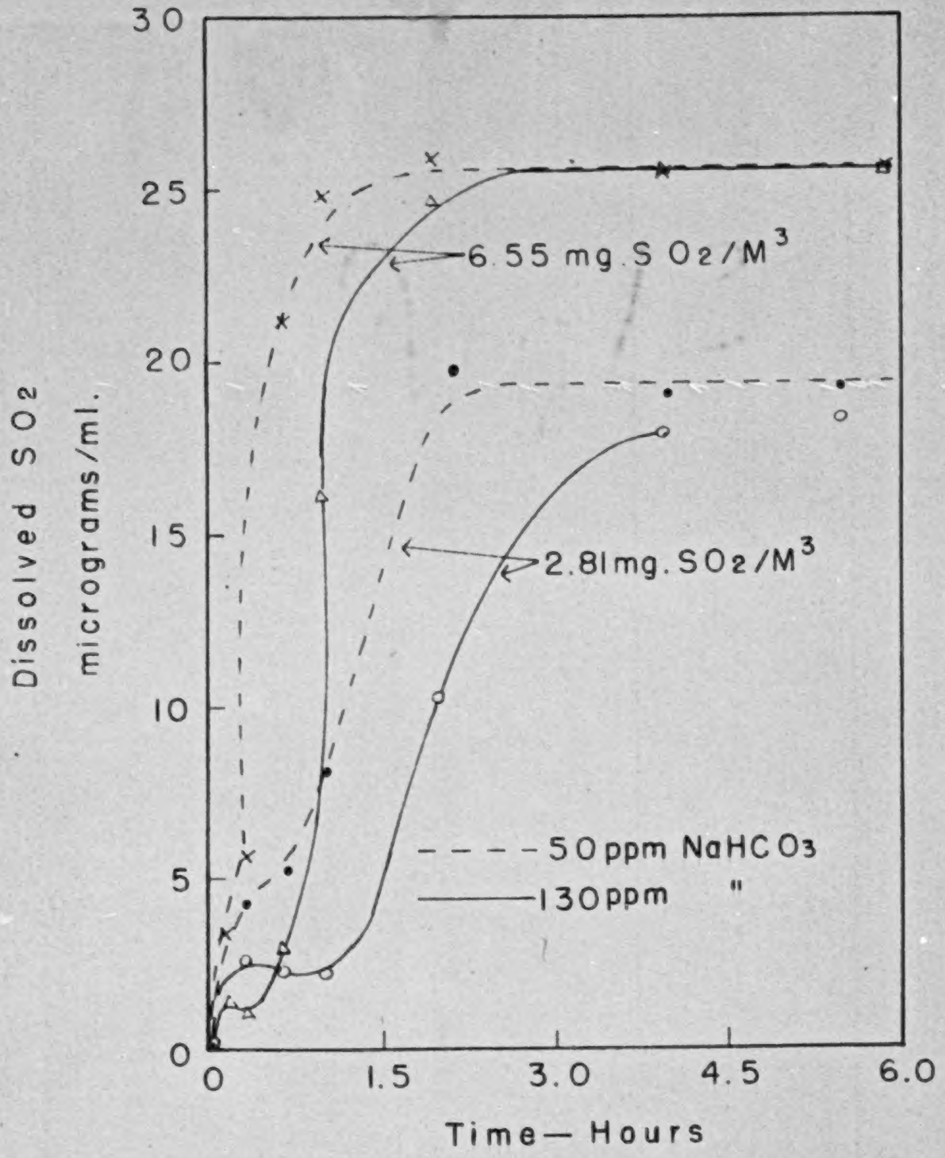

FIGURE 13 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN 3% SODIUM CHLORIDE SOLUTIONS CONTAINING 50 AND 130 ppm SODIUM BICARBONATE

# TABLE XI

## COMPARISON OF SOLUBILITIES OF ATMOSPHERIC SULFUR DIOXIDE IN SODIUM CHLORIDE AND SODIUM BICARBONATE SOLUTIONS EXPOSED FOR FOUR HOURS

| Air Conc. | Solubility (micrograms / ml.) | | | | |
|---|---|---|---|---|---|
| (mg. $SO_2/M^3$) | 3% NaCl | 50 ppm. $NaHCO_3$ | 130 ppm. $NaHCO_3$ | 50 ppm. $NaHCO_3$ + 3% NaCl | 130 ppm. $NaHCO_3$ + 3% NaCl |
| 2.81 | 8.0 | 32.5 | 39.0 | 19.3 | 18.0 |
| 6.55 | 13.2 | 39.0 | 65.0 | 25.5 | 25.5 |

The pH of the three percent sodium chloride solution containing 130 ppm. of sodium bicarbonate exposed to atmospheres containing 2.81 mg. $SO_2/M^3$ is presented in Figure 14. It can be seen that the pH value decreased very slowly during the first hour of exposure. During this same time the dissolved sulfur dioxide concentration increased for a short period of time then decreased to a minimum before it increased again. The slow decrease in pH value reflected the presence of the sodium bicarbonate acting as a buffer to prevent rapid changes in pH. After one hour the pH of the solution decreased rapidly and the amount of atmospheric sulfur dioxide that was dissolved increased rapidly.

One possibility for the decrease in the sulfur dioxide concentration in solution after a short period of exposure was the salting out of the gas by the sodium chloride that was in the solution. A study was conducted where both the sodium chloride and sodium bicarbonate content of the solutions were varied. Sodium chloride solutions of 1, 3 and 5 percent were prepared. To portions of each of the sodium chloride solutions sufficient sodium bicarbonate was added so that the resultant solutions contained 50 and 130 ppm. of sodium bicarbonate. Twenty ml. portions of these solutions were exposed in the test chamber to an atmospheric sulfur dioxide concentration of 3.27 mg./$M^3$.

Figure 15 shows the results of this study. The upper portion shows the curves for the rate of solution of atmospheric sulfur dioxide in 1, 3 and 5 percent sodium chloride solutions which contained 50 ppm. sodium bicarbonate. The slight rise in dissolved sulfur dioxide followed by a decrease in the amount of sulfur dioxide in solution was noted with all three salt concentrations. The decrease in the dissolved sulfur dioxide was more apparent in the solutions containing 130 ppm. sodium bicarbonate as shown in the lower portion of Figure 15. For almost one hour little or no sulfur dioxide was found in solution. The combination of sodium bicarbonate and sodium chloride depressed the solution of sulfur dioxide so that solutions containing 130 ppm. of sodium bicarbonate dissolved less atmospheric sulfur dioxide than those solutions which contained 50 ppm. of sodium bicarbonate.

The variations in pH observed with solutions containing sodium bicarbonate and sodium chloride did not show any unusual changes that could account for the effects noted on the solution of atmospheric sulfur dioxide. In some manner the presence of sodium chloride and sodium bicarbonate brought about a reaction with sulfur dioxide gas as it dissolved in a solution so that less sulfur dioxide was recovered in the solution after a period of exposure.

b) Phosphate-Sodium Chloride.--A study was conducted on the influence of phosphate and sodium chloride mixtures on the absorption of sulfur dioxide. Sufficient potassium hydrogen phosphate and potassium dihydrogen phosphate were added to a three percent sodium chloride solution so that each was $3 \times 10^{-4}M$ in the final solution. Twenty ml. portions of the mixed sodium chloride-phosphate solution were exposed in the test chamber to a concentration of 2.81 mg. $SO_2/M^3$.

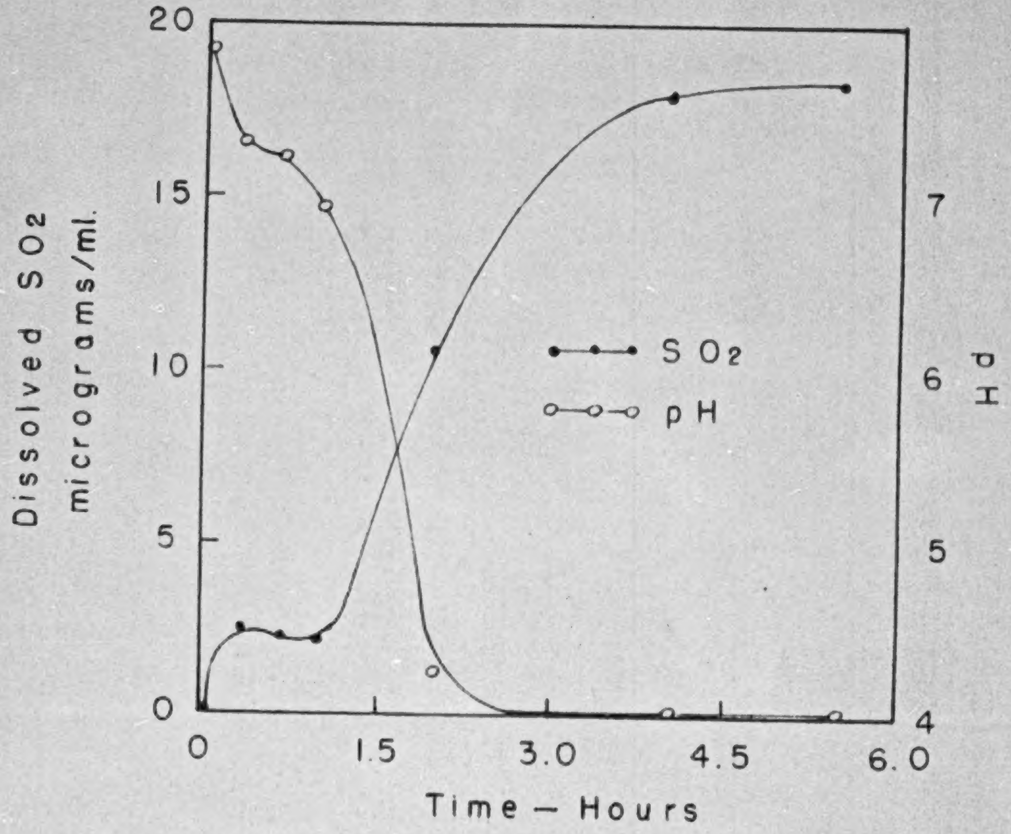

FIGURE 14 - pH OF 3% SALT SOLUTION CONTAINING 130 ppm $NaHCO_3$ EXPOSED TO AN ATMOSPHERE OF 2.81 mg. $SO_2/M3$

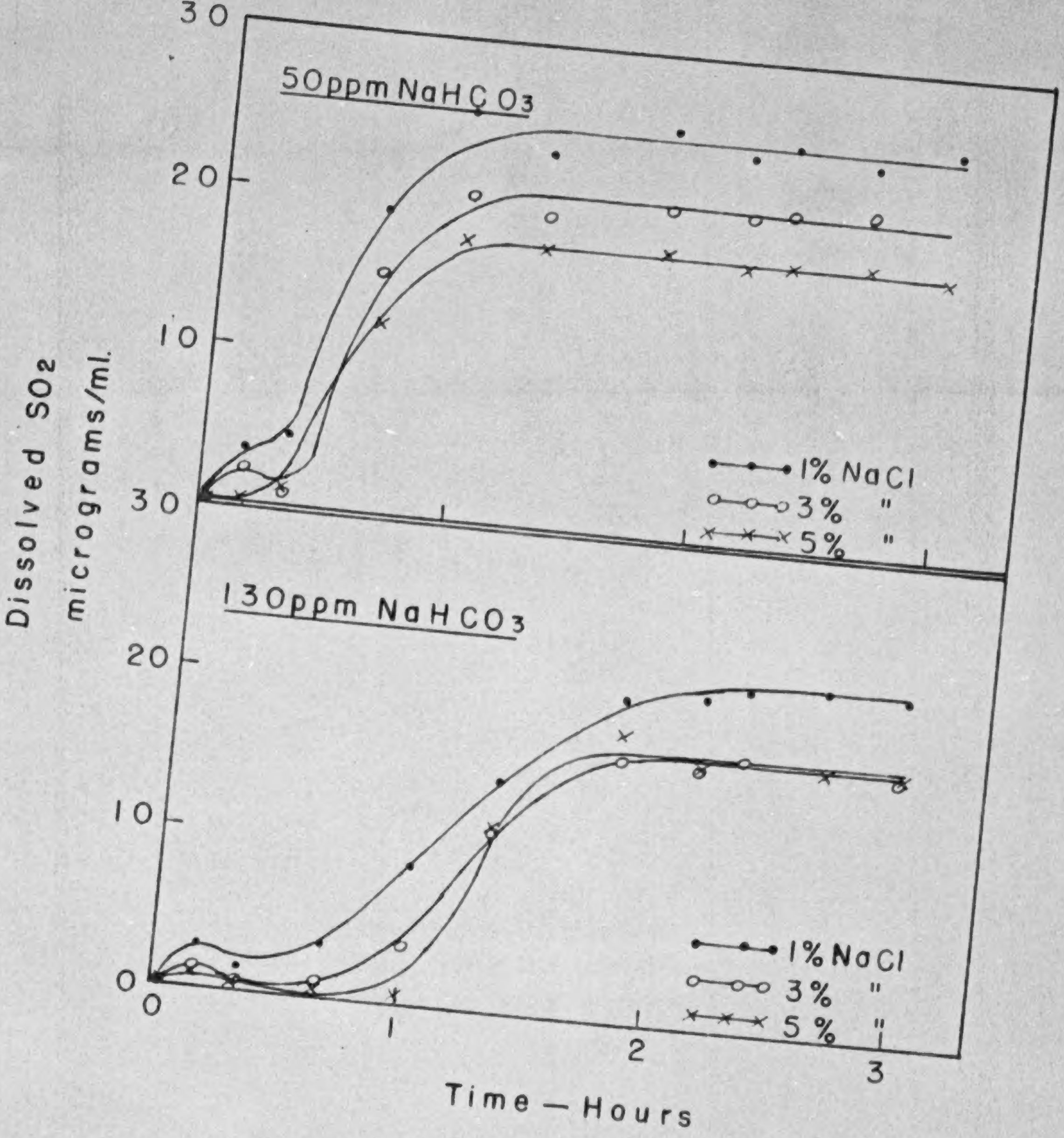

FIGURE 15 - RATE OF SOLUTION OF SULFUR DIOXIDE IN SODIUM CHLORIDE SOLUTIONS CONTAINING SODIUM BICARBONATE.

ATMOSPHERIC CONCENTRATION 3.27 mg. $SO_2/M^3$

The rate of solution of gaseous sulfur dioxide in the sodium chloride-phosphate solutions is shown in Figure 16, as well as the pH values of the solutions at the time of collection. A final saturation value of 19.90 micrograms $SO_2$/ ml. was obtained upon exposure to an atmosphere containing 2.81 mg. $SO_2/M^3$. The value obtained from Figure 17 for phosphate solutions exposed to the same concentration of sulfur dioxide is 20.50 micrograms $SO_2$/ ml. With the close agreement obtained for the final saturation value, it is apparent that the presence of three percent sodium chloride had very little effect on the solubility of atmospheric sulfur dioxide in the solution.

The discrepancy noted with the sodium chloride-sodium bicarbonate solutions and their absorption of sulfur dioxide was a characteristic of that system and not an effect noted whenever sodium chloride was present in the solution.

An overall comparison of the solubility of atmospheric sulfur dioxide in distilled water and the various water solutions after four hour exposure is shown in Figure 17. Sodium bicarbonate in solution increased the amount of atmospheric sulfur dioxide that dissolved as did the presence of phosphate in solution.

### 6. Natural Waters

a) Sea Water.--The absorption of atmospheric sulfur dioxide by the surface of the sea represents possibly one of the most important removal mechanisms in the fate of the gas. Studies were conducted to determine the rate of solution of the gas and the amount dissolved by a surface film of sea water exposed for four hours.

A sample of sea water was obtained off the coast at Asbury Park, New Jersey. The collected sample was filtered through glass wool to remove any large material and then stored in the dark until the time of use. A partial analysis of the sample is given in Table XII.

Twenty ml. portions of sea water were exposed to atmospheric sulfur dioxide in the test chamber for various periods of time.

Figure 18 shows the rate of solution of atmospheric sulfur dioxide in the sea water samples exposed in the test chamber. It can be seen that the solution of sulfur dioxide in sea water followed the same pattern as the solutions containing sodium bicarbonate in three percent sodium chloride. There was a rise in the amount of recovered sulfur dioxide in solution followed by a decrease after about one hour exposure. This in turn was followed by a rise to the final saturation value. The occurrence of the minumum took place at a later time when the atmospheric concentrations were lower. The sample exposed to only 0.95 mg. $SO_2/M^3$ did not reach a final saturation value after eight hours exposure although it had passed through a minimum and the recovered sulfite was increasing.

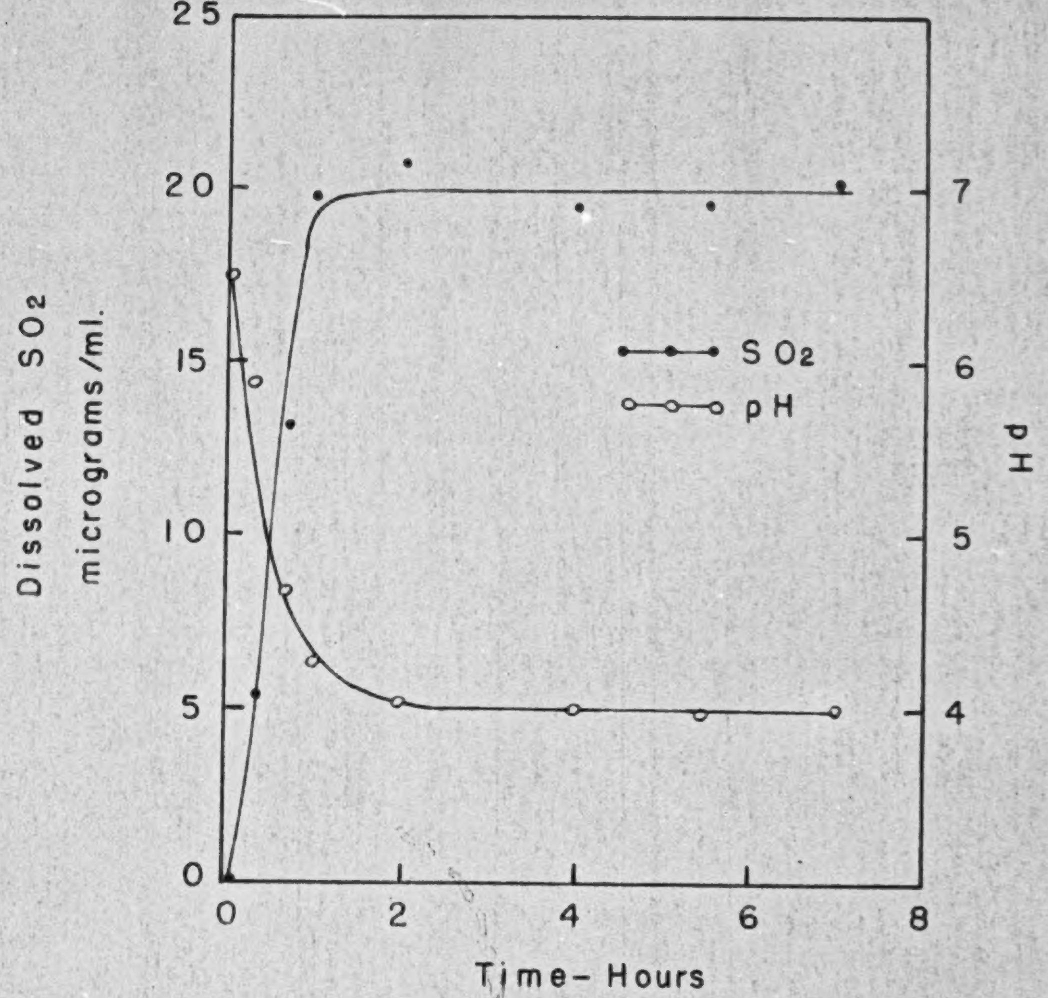

FIGURE 16 - pH OF 3% SODIUM CHLORIDE SOLUTION CONTAINING PHOSPHATE EXPOSED TO AN ATMOSPHERE OF 2.81 mg. $SO_2/M^3$

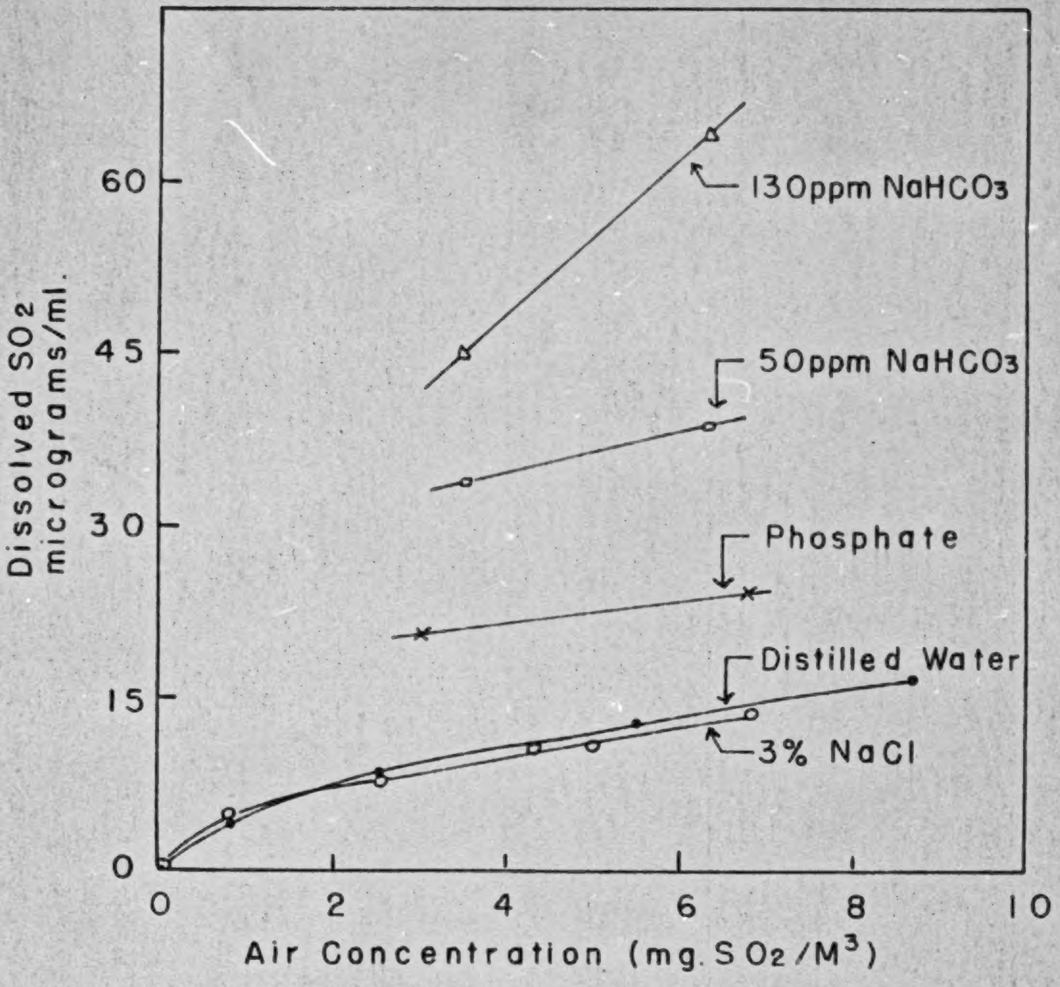

FIGURE 17 - COMPARISON OF SOLUBILITY OF ATMOSPHERIC SULFUR DIOXIDE IN VARIOUS AQUEOUS SOLUTIONS EXPOSED FOUR HOURS

## TABLE XII

## ANALYSIS OF SEA WATER SAMPLE - OBTAINED OCTOBER 4,1962, ASBURY PARK, NEW JERSEY

| Constituent | mg./1 |
|---|---|
| Total Solids | 34,980 |
| Chloride | 17,430 |
| Sulfate | 2,237 |
| Total Alkalinity | 92.5 (as $CaCO_3$) |
| Bicarbonate | 92.5 |
| pH | 7.78 |

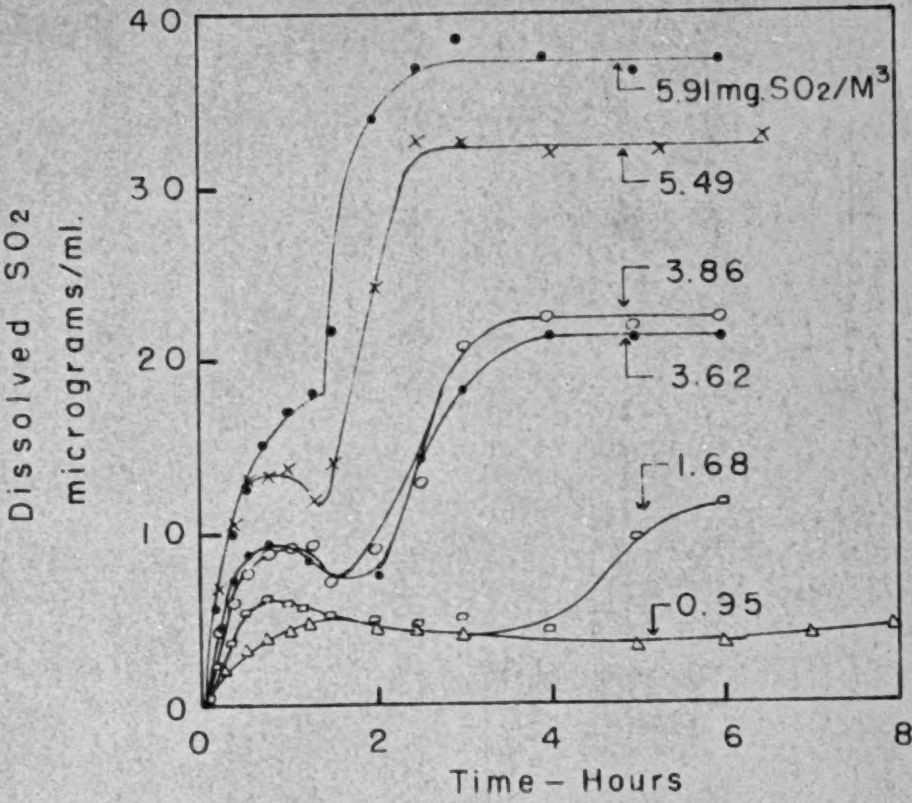

FIGURE 18 - RATE OF SOLUTION OF SULFUR DIOXIDE IN SEA WATER SAMPLES

The pH value of the sea water exposed to 1.68 mg. $SO_2/M^3$ is shown in Figure 19. The relative flat portion of the pH curve for the first three hours indicates a buffer region, probably due to the sodium bicarbonate that was present in the sea water. During this time period the recovered sulfur dioxide passed through the minimum. After this, a marked decrease in the pH accompanied the rapid rise in the solution of the gaseous sulfur dioxide. At the final saturation value of sulfur dioxide in solution the pH remained constant near a value of 4.0. The final pH value reached by all of the sea water samples exposed in the study ranged from 3.70 to 4.05.

b) Acid Lake Water.--A sample of water was obtained from Cranbury Lake, Cranbury, New Jersey. The pH of the water after sedimentation was found to be 4.70.

When samples of the lake water were exposed to an atmosphere containing 9.13 mg. $SO_2/M^3$ for four hours, only one microgram of sulfur dioxide could be found in the entire sample of lake water. Exposure to lower concentrations of atmospheric sulfur dioxide resulted in even lower recoveries of the dissolved gas. The low pH value of the original lake water (4.7) prevented significant absorption of the gas.

A comparison of the solubility of atmospheric sulfur dioxide in sea water and other aqueous solutions exposed four hours is given in Figure 20. The values for sea water fall between those for solutions containing three percent sodium chloride and the sodium bicarbonate solutions.

## 7. Discussion.

The absorption of atmospheric sulfur dioxide by water results in the formation of sulfurous acid which in turn is ionized in the solution. The equilibrium conditions that exist are given by the following equations:

$$SO_2 \text{ soln.} \quad H \; SO_2 \text{ gas} \qquad (1)$$

The partial pressure of $SO_2$ above the solution times a constant H is in equilibrium with the uncombined gas in the solution. The constant H is Henry's constant for the solution of gases. Rewriting equation 1:

$$SO_2 \text{ soln.} \quad Hp$$

The reactions in solution are:

$$H_2O + SO_2 \qquad H_2SO_3 \qquad (2)$$

$$H_2SO_3 \quad K_1 \quad H^+ \quad +HSO_3^- \qquad (3)$$

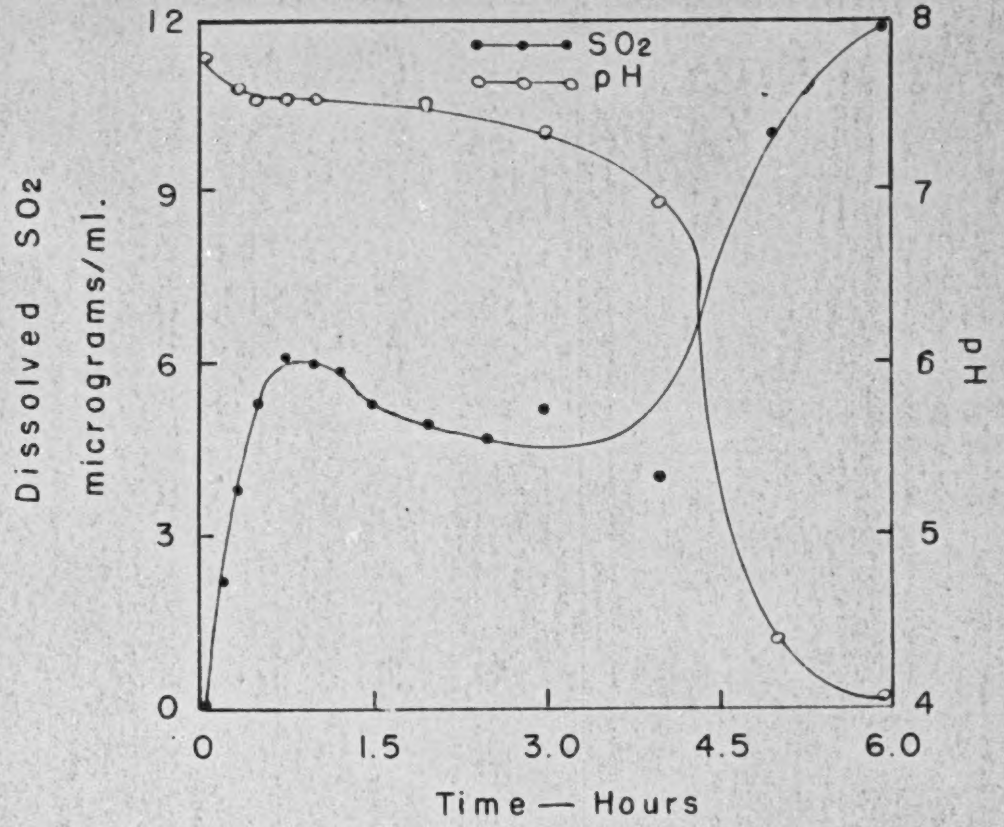

FIGURE 19 - pH OF SEA WATER SAMPLES EXPOSED TO 1.68 mg. $SO_2/M^3$

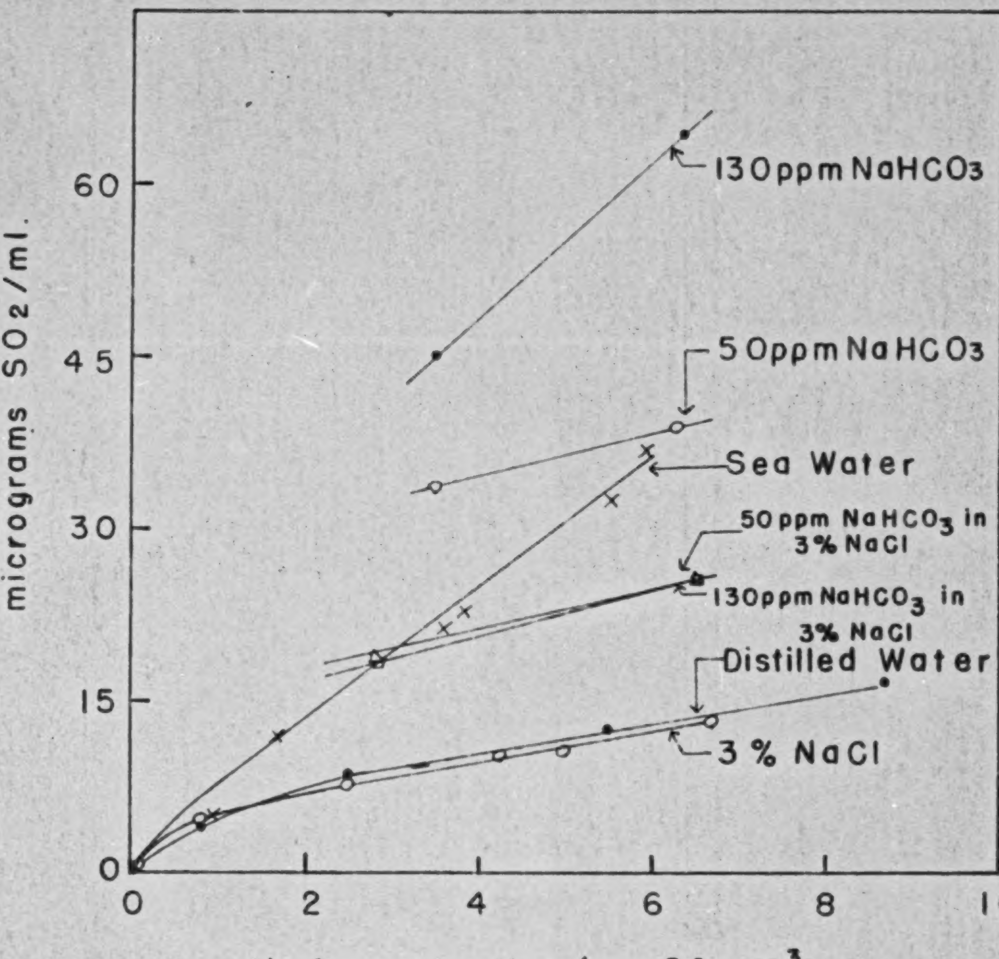

FIGURE 20 - COMPARISON OF SOLUBILITY OF ATMOSPHERIC SULFUR DIOXIDE IN VARIOUS AQUEOUS SOLUTIONS EXPOSED FOUR HOURS

$$HSO_3^- \qquad \overset{K_2}{\phantom{\rightleftharpoons}} \qquad H^+ \qquad SO_3^= \qquad (4)$$

The values of $K_1$ and $K_2$ are as follows:

$$K_1 = 1.7 \times 10^{-2}$$

$$K_2 = 5 \times 10^{-6}$$

With the great difference in the ionization constants, it can be assumed that equation 4 does not contribute appreciably to the pH of aqueous solutions of sulfur dioxide and that equation 3 represents the conditions that exist in the solution. If the amount of bisulfite can be determined for equation 3, then the amount of un-ionized sulfurous acid can be determined, and from this the value of H computed for equation 1, which would then show whether the solution of sulfur dioxide in water followed the law of partial pressures.

The information available is the total amount of sulfur dioxide in solution shown in Table VI and repeated in Table XIII, and the value for the ionization constant for sulfurous acid.

The relationships that are known are as follows:

$$H_2SO_3 \quad + \quad HSO_3^- \quad = \quad T \quad \text{(Total sulfite in solution)} \qquad (5)$$

$$\frac{H^+ \quad HSO_3^-}{H_2SO_3} = K_1 \qquad (6)$$

$$H^+ = HSO_3^- \qquad (7)$$

With these three equations it was possible to compute the value for amount of hydrogen ion in the solution and from equation 7 to compute the amount of bisulfite present.

Solution of the three simultaneous equations is as follows:

Substituting equation 7 in equation 6 gives:

$$\frac{H^+ \quad H^+}{H_2SO_3} = K_1 \qquad (8)$$

$$\frac{H^{+\,2}}{H_2SO_3} = K_1 \qquad (9)$$

Transforming equation 5 gives:

$$H_2SO_3 = T - HSO_3^- \qquad (10)$$

Substituting equation 7 into equation 10:

$$H_2SO_3 = T - H^+ \qquad (11)$$

Substituting equation 11 into equation 9:

$$\frac{H^{+\,2}}{T - H^+} = K_1 \qquad (12)$$

$$H^{+\,2} + K_1 \quad H^+ - K_1T = 0 \qquad (13)$$

Solution of the quadratic equation for the hydrogen ion concentration gave values for pH that could be compared to the measured values as well as the value for the amount of ionized bisulfite present in the solutions. The results are presented in Table XIII. A comparison of the calculated pH values versus the observed pH values shows very close agreement so that the assumption that the second ionization was not significant was correct.

From equation 7 the amount of bisulfite in solution was equal to the amount of hydrogen ion in the solution, and from equation 5 the amount of un-ionized sulfurous acid was equal to the total sulfite in solution minus the amount of bisulfite. Equation 1 states that, if the amount of un-ionized gas in solution is divided by the partial pressure, the air concentration, the result should be constant if the gas follows the law of partial pressure. Table XIII shows that for air concentrations ranging from 0.81 to 8.73 mg. $SO_2/M^3$ the solubility of un-ionized sulfurous acid does in fact follow the law of partial pressure. The column headed "H" shows the result of this calculation.

It can also be seen from this table that the un-ionized sulfurous acid in the solution represented only a very small fraction of the total sulfite in solution. Most of the sulfite in solution was present in the form of bisulfite. The concentration of bisulfite, which was equal to the hydrogen ion concentration shown on Table XIII, was 100 times the concentration of the un-ionized sulfurous acid.

The addition of phosphate to the water solutions showed an increase in the amount of dissolved sulfur dioxide in solution. The reaction that takes place is:

$$H_2SO_3 \quad + \quad HPO^{=} \qquad\qquad H_2PO_4^{-} \quad + \quad HSO_3^{-} \tag{14}$$

The expression for this equilibrium is:

$$K = \frac{H_2PO_4^{-} \qquad HSO_3^{-}}{H_2SO_3 \qquad HPO_4^{=}} = \frac{K_1}{K_2} \tag{15}$$

$$\frac{K_1}{K_2} = \frac{1.7 \times 10^{-2}}{2 \times 10^{-7}} = 8 \times 10^{4}$$

## TABLE XIII

### COMPARISON OF CALCULATED AND OBSERVED pH VALUES IN AQUEOUS SOLUTIONS AND COMPUTATION OF HENRY'S LAW CONSTANT

| Air Conc. | Soln. Conc. | $M\ SO_2/1$ | $M\ H^+/1$ | M un-ionized $H_2SO_3/1$ | pH | | H |
|---|---|---|---|---|---|---|---|
| ($mg.SO_2/M^3$) | (micrograms $SO_2/ml.$) | ($x\ 10^4$) | ($x\ 10^4$) | ($x\ 10^6$) | Cal. | Obs. | |
| 0.81 | 4.50 | 0.7031 | 0.7002 | 0.288 | 4.15 | 4.10 | 0.023 |
| 2.54 | 8.88 | 1.388 | 1.3768 | 1.12 | 3.86 | 4.00 | 0.028 |
| 5.54 | 12.83 | 2.005 | 1.9815 | 2.31 | 3.72 | 3.80 | 0.026 |
| 8.73 | 16.75 | 2.617 | 2.5779 | 3.91 | 3.59 | 3.70 | 0.028 |

$$H = \frac{\text{micrograms } SO_2/\text{ml. un-ionized}}{\text{mg. } SO_2/M^3 \text{ air conc.}}$$

where $K_1$ is the first ionization constant for sulfurous acid and $K_2$ is the second ionization of phosphoric acid. Each phosphate was added so that the final solution contained $3 \times 10^{-4}$M which reacted with the sulfurous acid according to equation 14. The total amount of sulfite shown in Table XIV is made up of ionized and un-ionized forms as follows:

$$T = H_2SO_3 + HSO_3^- \qquad (16)$$

Substituting in equation 15:

$$8 \times 10^4 = \frac{HSO_3{-} \quad 3 \times 10^{-4} \quad + \quad HSO_3^-}{T - HSO_3^- \quad 3 \times 10^{-4} \quad - HSO_3^-} \qquad (17)$$

Solution of equation 17 for the bisulfite gives the amount that reacted with the phosphate. The sulfite in excess of this amount dissolves in water according to equation 3, and by means of equation 13 it is possible to calculate the pH of the resulting solution. The results are presented in Table XIV.

The addition of sodium bicarbonate to the solution also increased the amount on sulfur dioxide dissolved in solution. The reaction that takes place is:

$$H_2SO_3 + HCO_3^- \qquad H_2CO_3 + HSO_3^- \qquad (18)$$

The expression for this equilibrium is:

$$K = \frac{H_2CO_3 \quad HSO_3^-}{H_2SO_3 \quad HCO_3^-} = \frac{K_1}{K_2} \qquad (19)$$

where $K_1$ is the first ionization constant for sulfurous acid and $K_2$ is the first ionization constant for carbonic acid.

$$\frac{K_1}{K_2} - \frac{1.7 \times 10^{-2}}{3.7 \times 10^{-7}} = 0.45 \times 10^5$$

# TABLE XIV

## COMPARISON OF OBSERVED AND CALCULATED pH VALUES OF PHOSPHATE SOLUTIONS EXPOSED TO ATMOSPHERIC SULFUR DIOXIDE

| Air Conc. (mg. $SO_2$/M$^3$) | Soln. Conc. (micrograms $SO_2$/ml.) | Phosphate (moles/1 x $10^4$) | $SO_2$ in Soln. (moles/1 x $10^4$) | Excess $SO_2$ (moles/1 x $10^4$) | pH | |
|---|---|---|---|---|---|---|
| | | | | | Cal. | Obs. |
| 3.00 | 21.00 | 3 | 3.28 | 0.28 | 4.54 | 4.55 |
| 6.71 | 24.45 | 3 | 3.82 | 0.82 | 4.09 | 4.18 |

The reaction proceeds far to the right, therefore it can be assumed that all of the bicarbonate reacts on mole for mole basis with the sulfur dioxide. A check of the recovered sulfur dioxide in the solutions exposed to atmospheric concentrations of the gas showed that there was less sulfur dioxide in solution than could be accounted for by reaction with the bicarbonate. In the bicarbonate solutions there was the possibility of loss of carbon dioxide from the solution upon acidification. A discrepancy was found in recovered sulfur dioxide where sodium bicarbonate-sodium chloride solutions were exposed to atmospheric sulfur dioxide. The recoveries were lower with increased amounts of bicarbonate in solution. It is possible that an evolution of carbon dioxide took place that changed the partial pressure of the gases over the surface of the exposed liquid. This would have the effect of changing the rate and extent of solution of the gas. Another mechanism which might account for the loss of sulfur dioxide from the system would be the mechanical scrubbing of gas from the solution by evolution of carbon dioxide and the removal of some of the dissolved sulfur dioxide leading to apparent low recoveries of the gas in solution.

The same type of reaction was noted when sea water was exposed to atmospheric sulfur dioxide. In this case again sodium bicarbonate and sodium chloride were present in the solution and the recovered sulfur dioxide showed a minimum for the first hour before the rate of solution increased in the normal manner.

The results presented here did not suggest any definite reaction that was taking place in solutions containing sodium bicarbonate, but it was noted that the systems that did not follow the expected patterns of solution all contained sodium bicarbonate. The possibility of evolution of carbon dioxide was present in all of these cases and the possible effect on the solution of sulfur dioxide was not determined in these studies.

It has been shown that the solubility of sulfur dioxide followed the law of partial pressure for only the un-ionized portions of the gas in a solution. The remainder of the gas that dissolved reacted with the water and ionized to form bisulfite. The law of partial pressures did not describe the amount of sulfite found in solution. It was found, however, that a simple exponential relationship could be used to describe the solubility of atmospheric sulfur dioxide over the concentration range of 0.81 to 8.73 mg./$M^3$. A general equation of this type has the form:

$$S = K C^a$$

where "S" is the concentration of sulfite in solution, "C" is the atmospheric concentration of the gas, and "a" and "K" are proportionality constants. The log form of the equation is:

$$\text{Log } S = \text{Log } K + a \text{ Log } C$$

which is the equation of a straight line. A plot of "S" and "C" for distilled water, three percent sodium chloride solutions, and sea water is given in Figure 21. It can be seen that the exponential form of the equation can be used to describe the solubility of atmospheric sulfur dioxide in aqueous solutions. Values for the constants "a" and "K" were obtained for all of the aqueous solutions tested. Knowing the atmospheric concentration of sulfur dioxide and the two constants it is possible to predict the solubility of the gas in the various solutions. A listing of the constants and the predicted solubility in solutions exposed four hours to an atmospheric concentration of 2.70 mg./$M^3$ is presented in Table XV. The selection of 2.70 mg. $SO_2/M^3$ was only for purposes of comparison and the solubility at any other atmospheric concentration could be calculated with the constants listed in Table XV.

The data in Table XV indicate that three percent sodium chloride did not essentially change the solubility of atmospheric sulfur dioxide in the solutions. The presence of phosphate buffers increased the solubility of the gas by an amount equal to the amount of the buffer present in the solution. Bicarbonates also increased the solubility of the gas but less than was expected from the amount of buffer present in the solution. At an atmospheric concentration of 2.70 mg. $SO_2/M^3$ a four fold increase in the amount of dissolved sulfur dioxide was found when 50 ppm of sodium bicarbonate was present and this increased to five fold when the solution contained 130 ppm. of sodium bicarbonate.

Sodium bicarbonate-sodium chloride mixtures showed an increased solubility but not to the extent as the increases noted with sodium bicarbonate alone. Sea water also had greater solubility than distilled water or three percent sodium chloride, probably due to the presence of bicarbonates in the water.

## B. Adsorption of Sulfur Dioxide by Soils

### 1. General.

The removal of atmospheric sulfur dioxide by soil surfaces was considered to be significant in a study of the fate of the gas after emission to the atmosphere. Superimposed on this was the influence of soil moisture on the amount of gas adsorbed by a quantity of soil.

The exchange of gases, such as oxygen and carbon dioxide, has been studied in detail by a number of investigators (56, 63), but very little has been done regarding the up-take of atmospheric sulfur dioxide by soils. Fortman (26) stated that soils in the vicinity of industrial areas have a high acidity due to the adsorption of sulfur dioxide. Alway, Marsh, and Methly (1) found that soil samples exposed in the field did adsorb atmospheric sulfur dioxide.

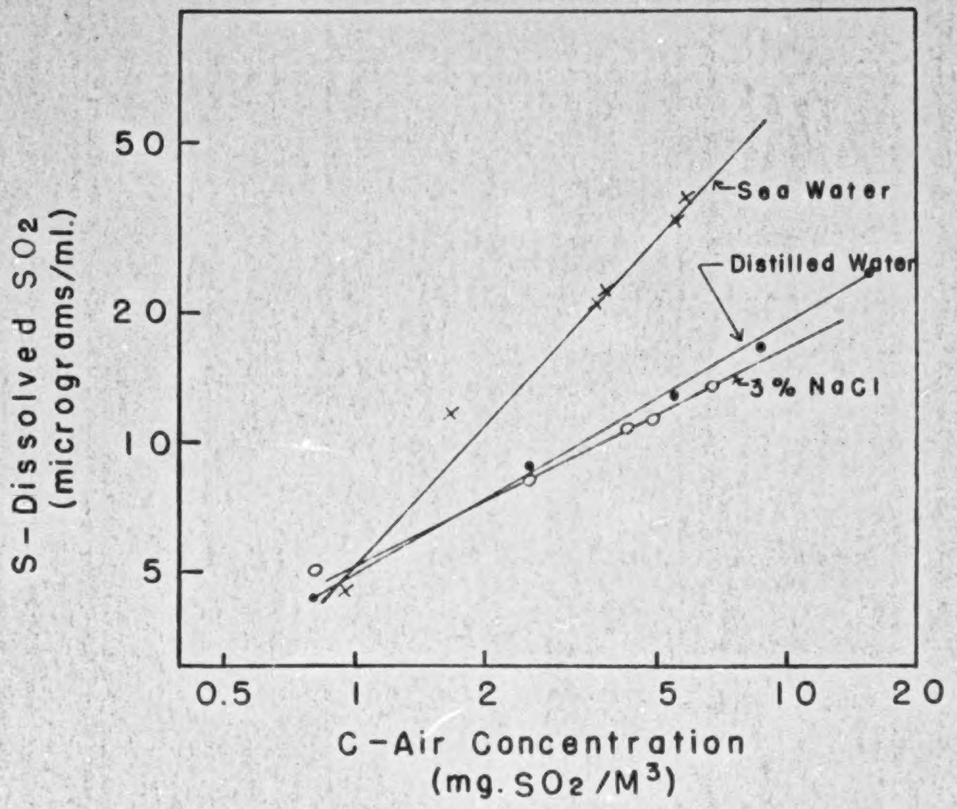

FIGURE 21 - SOLUBILITY OF ATMOSPHERIC SULFUR DIOXIDE IN AQUEOUS SOLUTIONS EXPOSED FOUR HOURS

### TABLE XV

### PARAMETERS FOR THE SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN WATER SOLUTIONS EXPOSED FOUR HOURS ($25^{o}C$)

| Solution | a | K | S- At 2.70 mg. $SO_2/M^3$ (micrograms/ml.) |
|---|---|---|---|
| Distilled water | 0.595 | 4.9 | 8.7 |
| 3% Sodium Chloride | 0.505 | 5.1 | 8.5 |
| Sea Water | 1.100 | 5.0 | 15.0 |
| 50 ppm. Sodium Bicarbonate | 0.235 | 25.3 | 32.0 |
| 130 ppm. Sodium Bicarbonate | 0.330 | 29.5 | 40.8 |
| Phosphate | 0.184 | 17.0 | 20.4 |
| 50 ppm. Sodium Bicarbonate in 3% Sodium Chloride | 0.301 | 14.0 | 18.8 |
| 130 ppm. Sodium Bicarbonate in 3% Sodium Chloride | 0.405 | 11.6 | 17.0 |

A study was undertaken to quantitate the up-take of atmospheric sulfur dioxide by two types on New Jersey soils: the Nixon type and the Lakewood type. The Lakewood soil representing a very acid soil, while the Nixon had a more normal acidity for soil in this area. The influence of soil moisture on the adsorption of atmospheric sulfur dioxide also was measured.

The two samples of soil were obtained from the Soils Department, Rutgers - The State University. An analysis of the soil samples is presented in Table XVI.

### 2. Procedure.

Glass columns 1.85 cm. in diameter and 15 cm. long were used to hold the soil samples. Air was drawn from the test chamber through two of these columns. One column contained the soil samples and the other served as a control. The effluent from the columns was passed into a fritted glass bubbler that contained sodium tetrachloromercurate solution. The pairs of samples obtained were analyzed by the colorimetric method, and the difference in recovery represented the amount of sulfur dioxide adsorbed by the soil. Each sample was collected at a rate of three liters/minute for 20 minutes. In this manner 60 liters of air containing sulfur dioxide passed through the columns in each sample.

This procedure was repeated for several atmospheric concentrations of sulfur dioxide and for several levels of soil moisture.

### 3. Results.

a) Dry Soils.--Before the study on the soil was conducted, the two columns were compared without a soil sample and the results are given in Table XVII.

The values shown in Table XVII indicated that the two columns gave comparable results. Any variations noted when a soil sample was present were ascribed to the adsorption of the atmospheric sulfur dioxide by the soil.

## TABLE XVI

## ANALYSIS OF TWO NEW JERSEY SOILS

| Constituent | Lakewood Soil | Nixon Soil |
|---|---|---|
| 1. Typical Mechanical Analysis (%) | | |
| Sand | 95 | 65 |
| Silt | 3 | 20 |
| Clay | 2 | 15 |
| 2. Volatile Matter (%) | 0.96 | 2.49 |
| 3. Moisture (%) | 0.053 | 0.52 |
| 4. Cation Exchange Capacity (me./100 gms.) | 2.5 | 7.5 |
| 5. Density (gm./ml.) | 2.53 | 2.46 |
| 6. Bulk Density (gm./ml.) | 1.55 | 1.39 |
| 7. pH | 4.0 | 5.5 |

## TABLE XVII

## COMPARISON OF RECOVERY OF SULFUR DIOXIDE IN COLUMNS WITHOUT SOIL SAMPLES

|  | mg. $SO_2/M^3$ |  |
|---|---|---|
| Number | Column 1 | Column 2 |
| 1 | 5.55 | 5.70 |
| 2 | 5.63 | 5.82 |
| 3 | 5.55 | 5.50 |
| 4 | 5.73 | 5.51 |
| 5 | 5.40 | 5.38 |
| 6 | 5.70 | 5.58 |
| 7 | 5.47 | 5.51 |
| 8 | 5.22 | 5.21 |
| Average | 5.53 ± 0.17 | 5.53 ± 0.18 |

The results of the adsorption of sulfur dioxide by ten grams of Nixon soil containing only 0.52 percent moisture are shown in Figure 22. Successive samples have been paired for ease of handling. The concentration of gas in the effluent is the average concentration of two successive samples. The difference between the influent concentration and the values shown on Figure 22 represent the amount of sulfur dioxide adsorbed by the soil. For the four influent atmospheric concentrations, the total amount of sulfur dioxide applied to the soil in each of the pairs of successive 60 liter samples was 405, 566, 1022, and 1134 respectively. Knowing the influent concentration and the effluent concentration, it was possible to compute the amount of sulfur dioxide retained by the soil for each volume of air that passed through the soil. This is shown in Table XVIII which presents the amount of sulfur dioxide retained by the Nixon soil from each 120 liters of sulfur dioxide containing air that was passed through the sample. The amount of sulfur dioxide indicated for the control sample was the total amount of sulfur dioxide applied to the soil in each 120 liters of air.

The adsorption of sulfur dioxide by Nixon soil was very rapid at the beginning for all concentrations used. Continued passage of sulfur dioxide through the soil resulted in less retention of the gas on the soil and greater quantities passed through. This indicated a saturation of the soil and an approach to a limiting value of adsorption.

Similar studies with ten grams of air dried Lakewood soil showed that no measureable amount of sulfur dioxide was adsorbed by the soil within the limits of the test as described. It, therefore, was impossible to construct a Figure which showed the adsorption by Lakewood soil.

The application of exponential equations for adsorption of atmospheric sulfur dioxide has been shown by Bienstock et al. (8) to be a satisfactory method for expressing adsorption of the gas by a variety of solid materials. The Freundlich equation applied to the adsorption on sulfur dioxide by soils has the general form:

$$\frac{X}{M} = K\,C^{\frac{1}{n}}$$

where; X = weight of sulfur dioxide retained by the soil

M = weight of soil

K and $\frac{1}{n}$ = proportionality constants

C = sulfur dioxide concentration in the effluent from the soil.

The log form of the equation is:

$$\text{Log}\ \frac{X}{M} = \text{Log}\ K + \frac{1}{n}\ \text{Log}\ C$$

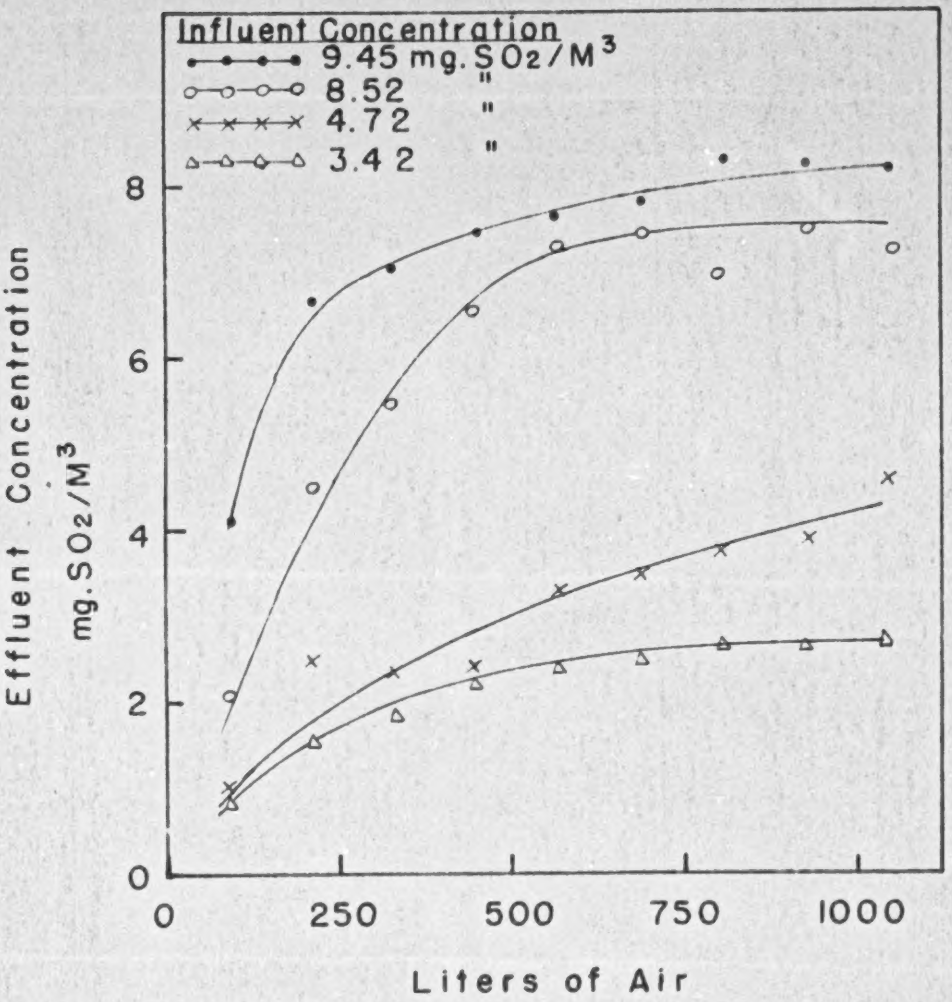

FIGURE 22 - ADSORPTION OF ATMOSPHERIC SULFUR DIOXIDE BY 10 GRAMS OF DRY NIXON SOIL

## TABLE XVIII

## RETENTION OF SULFUR DIOXIDE BY TEN GRAMS OF NIXON SOIL

| Sample Number | Sulfur Dioxide Retained (micrograms) | | | |
|---|---|---|---|---|
| Control ($SO_2$ applied) | 410 | 566 | 1,022 | 1,134 |
| 1 | 308 | 445 | 771 | 638 |
| 2 | 225 | 266 | 458 | 327 |
| 3 | 193 | 284 | 369 | 289 |
| 4 | 144 | 278 | 222 | 237 |
| 5 | 122 | 168 | 146 | 217 |
| 6 | 109 | 144 | 126 | 185 |
| 7 | 96 | 102 | 184 | 138 |
| 8 | 97 | 99 | 120 | 159 |
| 9 | 74 | 32 | 152 | 105 |

The values for the constants K, which is the intercept when C is equal to 1, and $\frac{1}{n}$, which is the slope, can be obtained from a plot of Log $\frac{X}{M}$ versus Log C which, according to the equation, should be a straight line. Figure 23 shows the Freundlich adsorption isotherm for atmospheric sulfur dioxide on Nixon soil was a straight line and, therefore, the equation can be used to describe the adsorption by Nixon soil.

The value for K obtained from Figure 23 is 90, and $\frac{1}{n}$ is equal to 0.576. By means of the Freundlich equation and using the two constants, it was possible to predict the amount of sulfur dioxide that would be retained by a sample of Nixon soil for any concentration of the gas. This was used to measure the influence of soil moisture on adsorption of atmospheric sulfur dioxide.

The Nixon soil sample that had been exposed to 9.45 mg. $SO_2/M^3$ of air was sealed from the atmosphere and allowed to stand for five days. After the five-day period, air containing sulfur dioxide, was drawn through the soil sample. The air samples were taken at three liters per minute for 20 minutes. In a series of air samples taken consecutively it was found that the first two samples had relatively high adsorptive capacities, but not as high as the original soil samples which had not been subjected previously to atmospheres containing sulfur dioxide. By the fifth air sample, however, the adsorptive capacity returned to the same low level that it had attained after prolonged exposure to the gas. The soil had shown some regenerative power with increased adsorption after the five-day holding period but not a complete restoral of the original adsorptive capacity. It was not possible to determine the time required for complete regeneration of the adsorptive power on the Nixon soil, or to determine whether the adsorptive capacity was ever completely regenerated.

b) Soil Moisture.--The influence of soil moisture was measured by passing a uniform concentration of sulfur dioxide through soil samples of various moisture content. Nixon soil samples containing 2, 5, and 10 percent moisture were prepared by adding the required amount of water to ten grams of the soil. In this manner the amount of soil used was constant and only the water content changed. The concentration of sulfur dioxide in the influent air was 6.03 mg. $SO_2/M^3$.

By means of the Freundlich equation and using the constants previously determined, it was computed that 1,134 micrograms of sulfur dioxide would be removed from 600 liters of air containing 6.03 mg. $SO_2/M^3$ by ten grams of soil. The influence of soil moisture on the adsorption by Nixon soil is shown in Table XIX.

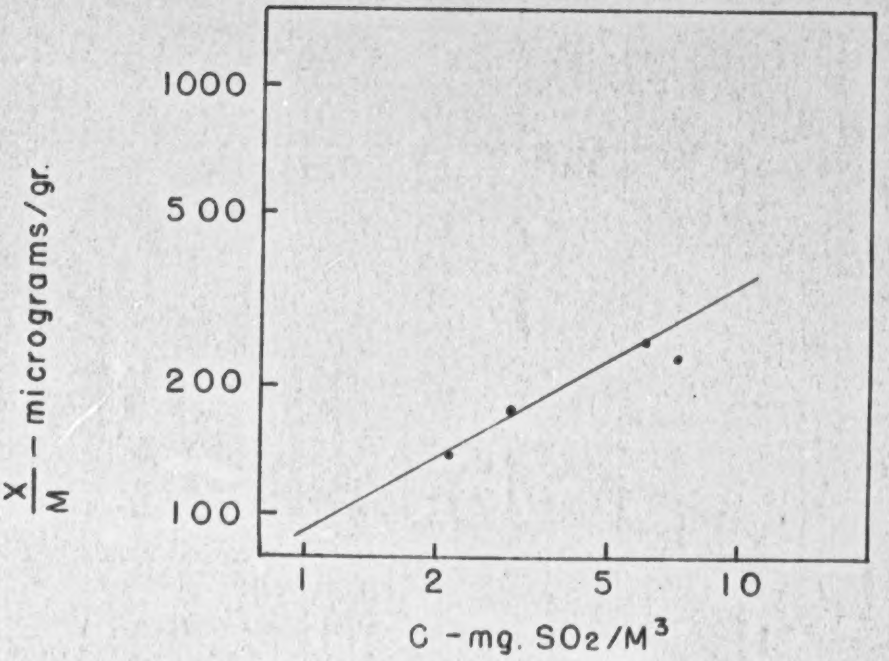

FIGURE 23 - FREUNDLICH ADSORPTION ISOTHERM FOR

SULFUR DIOXIDE ON NIXON SOIL

## TABLE XIX

## ADSORPTION OF SULFUR DIOXIDE BY 10 GRAMS OF NIXON SOIL

| Influent Concentration (mg. $SO_2M^3$ | Air Volume (liters) | Moisture (%) | Micrograms Adsorbed |
|---|---|---|---|
| 6.03 | 600 | 0.52 | 1,134* |
| 6.03 | 600 | 2.0 | 1,908 |
| 6.03 | 600 | 5.0 | 2,885 |
| 6.03 | 600 | 10.0 | 2,909 |

*Calculated from Freundlich equation

The adsorption of atmospheric sulfur dioxide by ten grams of Nixon soil increased from 1,134 micrograms to 1,908 micrograms when the soil moisture was 2 percent. Five percent moisture increased the adsorption to 2,885 micrograms and the value for 10 percent was found to be 2,909 micrograms of sulfur dioxide. The results are shown in Figure 24, where it can be seen that moisture markedly increased the amount of sulfur dioxide adsorbed by the Nixon soil. As the moisture content increased, however, the amount adsorbed tended to level off so that increased soil moisture did not bring about further increases in the amount of sulfur dioxide retained by the soil.

Adsorption isotherms could not be constructed for the Lakewood soil, therefore, only a graphic comparison was made to show the influence of soil moisture. Figure 25 shows the adsorption by 25 grams of Lakewood soil to which had been added 2, 5, and 10 percent moisture. The effluent from the soil samples and the control were collected and analyzed in the same manner as that used on the Nixon soil.

While the dry Lakewood soil did not have an adsorptive capacity for atmospheric sulfur dioxide, Figure 25 shows that the presence of moisture did increase the adsorption of the gas by Lakewood soil. It can be seen that the Lakewood soil sample with 10 percent moisture adsorbed more sulfur dioxide than the sample with 5 percent moisture, which in turn adsorbed more than a sample with only 2 percent moisture.

It has been shown that soil moisture increased the amount of sulfur dioxide adsorbed by a soil sample. The extent to which the soil influenced the adsorption of the gas by the water present in the soil is shown in Table XX.

The presence of soil had a profound effect on the solubility of atmospheric sulfur dioxide in water. Ten grams of Nixon soil increased the amount of sulfur dioxide found in distilled water from 14.4 to 1,775 micrograms for 1.11 ml. of water. The addition of 130 ppm. of sodium bicarbonate to distilled water only increased the solubility in 1.11 ml. of water to 68.7 micrograms. With the Lakewood soil 25 grams of soil were tested and 2.78 ml. of water was added to the soil sample to bring the moisture content up to 10 percent. Twenty-five grams of Lakewood soil increased the amount of sulfur dioxide dissolved in 2.78 ml. of water from 41.4 to 470 micrograms. The addition of 130 ppm. of sodium bicarbonate to distilled water only increased the solubility in 2.78 ml. of water to 198.2 micrograms.

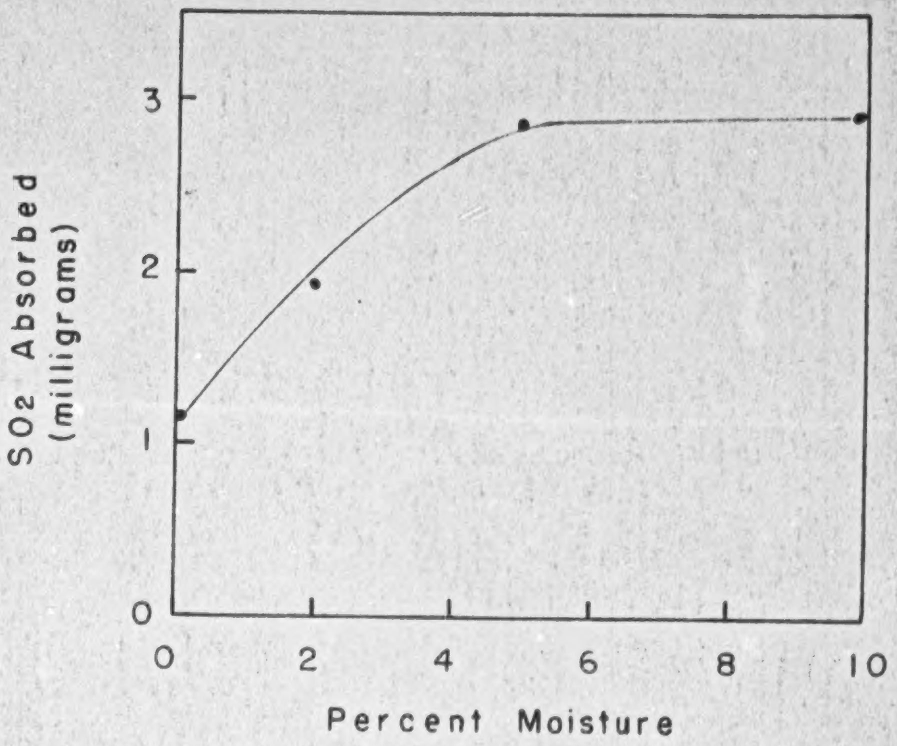

FIGURE 24 - INFLUENCE OF MOISTURE ON THE ADSORPTION OF SULFUR DIOXIDE BY 10 GRAMS OF NIXON SOIL.
AIR CONCENTRATION 6.03 mg. $SO_2/M^3$.
AIR VOLUME - 600 LITERS

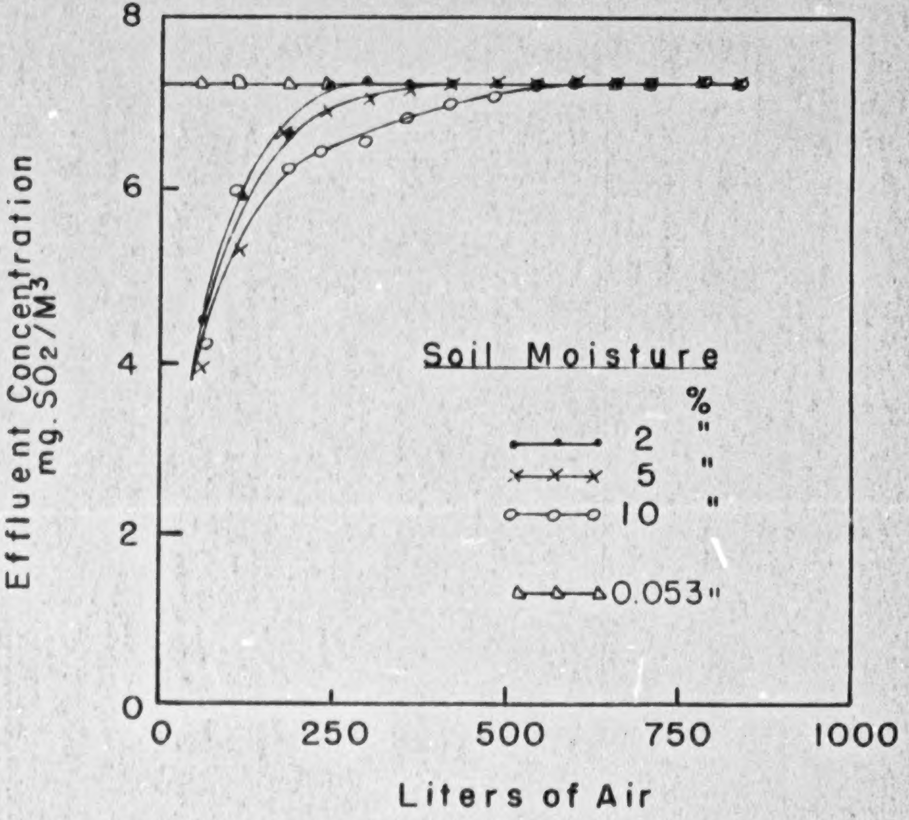

FIGURE 25 - ABSORPTION OF ATMOSPHERIC SULFUR DIOXIDE BY 25 GRAMS OF MOISTENED LAKEWOOD SOIL.

INFLUENT CONCENTRATION 7.27 mg. $SO_2/M3$.

## TABLE XX

### COMPARISON OF THE AMOUNT OF SULFUR DIOXIDE ABSORBED BY WATER MIXED WITH SOIL AND SOME WATER SOLUTIONS ALONE

| Water Solution | ml. of Water | Air Concentration (mg. $SO_2/M^3$) | Total $SO_2$ Absorbed (micrograms) |
|---|---|---|---|
| Mixed with 10 grams of Nixon soil | 1.11 | 6.03 | 1,775 |
| Distilled water | 1.11 | 6.03 | 14.4 |
| 3% NaCl | 1.11 | 6.03 | 14.0 |
| Sea water | 1.11 | 6.03 | 39.6 |
| 130 ppm. $NaHCO_3$ | 1.11 | 6.03 | 68.7 |
| Mixed with 25 grams of Lakewood soil | 2.78 | 7.27 | 470 |
| Distilled water | 2.78 | 7.27 | 41.1 |
| 3% NaCl | 2.78 | 7.27 | 40.0 |
| Sea water | 2.78 | 7.27 | 123.0 |
| 130 ppm. $NaHCO_3$ | 2.78 | 7.27 | 198.2 |

Normally sulfur-dioxide-rich air passes over a soil and not through it as was done in this test. In this way only penetration from the surface is effective in removal of the gas from the air. A laboratory study was conducted to simulate these conditions.

Ten grams of the Nixon and Lakewood soils were placed in small horizontal containers so that the air passed over the surface of the soil. A control sample containing no soil was used to measure the amount of sulfur dioxide passed over the soil, and this was used to compute the amount of sulfur dioxide removed by the soil surface. The study was extended to include the influence of moisture on the adsorption.

The ten gram samples of soils were placed in a container so that 13.3 sq. cm. of soil was exposed to the air.

Figure 26 shows the adsorption by 13.3 sq. cm. of Nixon soil. It can be seen that the adsorption that took place on the dry soil increased with increasing amount of water. The removal of sulfur dioxide partakes of two phenomena; one, of adsorption on the soil materials itself, and the other, the solubility in the water that is present.

From Figure 27, which shows the adsorption of atmospheric sulfur dioxide by 13.3 sq. cm. of Lakewood soil, it can be seen that the presence of moisture increased the amount of sulfur dioxide taken up by the soil. Dry Lakewood soil did not adsorb any of the gas, but as the amount of water in the soil increased, the amount of sulfur dioxide removed from the air increased. With the Lakewood soil adsorption on the soil material was not very significant, but the solubility of sulfur dioxide in the soil moisture is significant.

Total removals shown in Figures 26 and 27 for the untreated and treated soils exposed to the gas are given in Table XXI.

It can be seen that soil moisture had a marked influence on the adsorption of sulfur dioxide by soils. The presence of 10 percent moisture in the Nixon soil more than doubled the amount retained by 13.3 sq. cm. of that soil. The increase was even more striking with the Lakewood soil, although the magnitude was not as great as the Nixon soil. In this case 10 percent moisture increased the adsorption from an unmeasureable amount to over 100 micrograms.

The influence of the soil on the solubility of the gas in water is shown on Table XXII. It can be seen that the presence of soil greatly increased the solubility of sulfur dioxide in water. The results shown in Table XXII are surface exposures of soils with 10 percent moisture. The presence of ten grams of Nixon soil increased the amount of sulfur dioxide

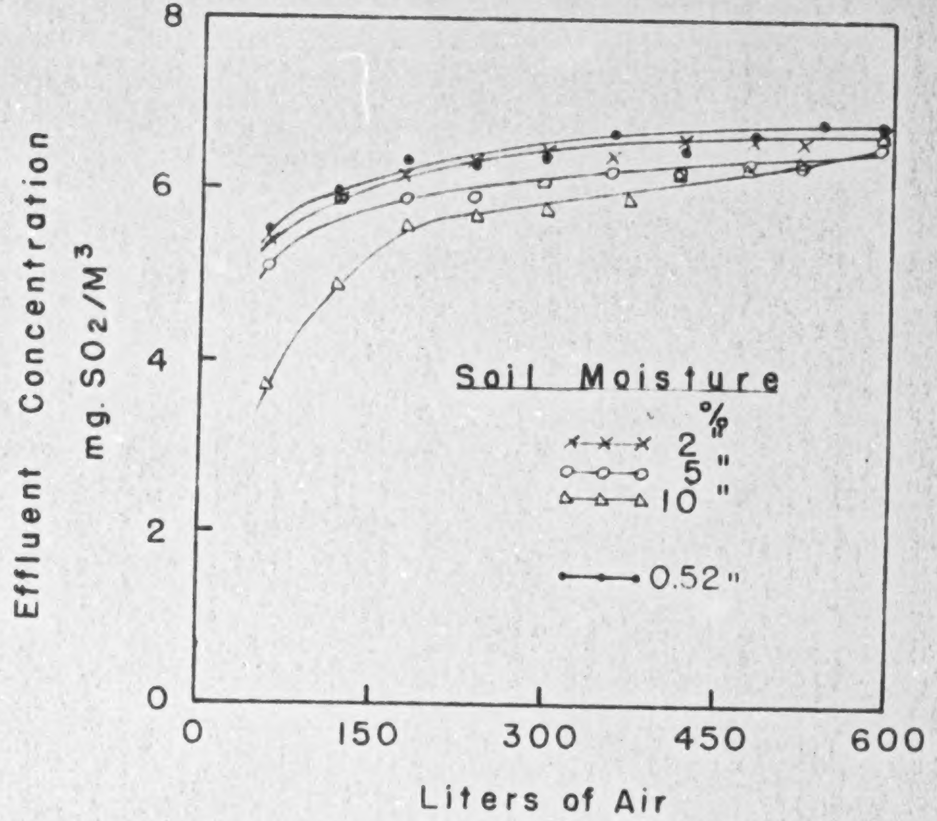

FIGURE 26 - ADSORPTION OF ATMOSPHERIC SULFUR DIOXIDE BY 13.3 sq. cm. OF NIXON SOIL.

TOTAL SOIL 10 GRAMS

INFLUENT CONCENTRATION 6.87 mg. $SO_2/M^3$.

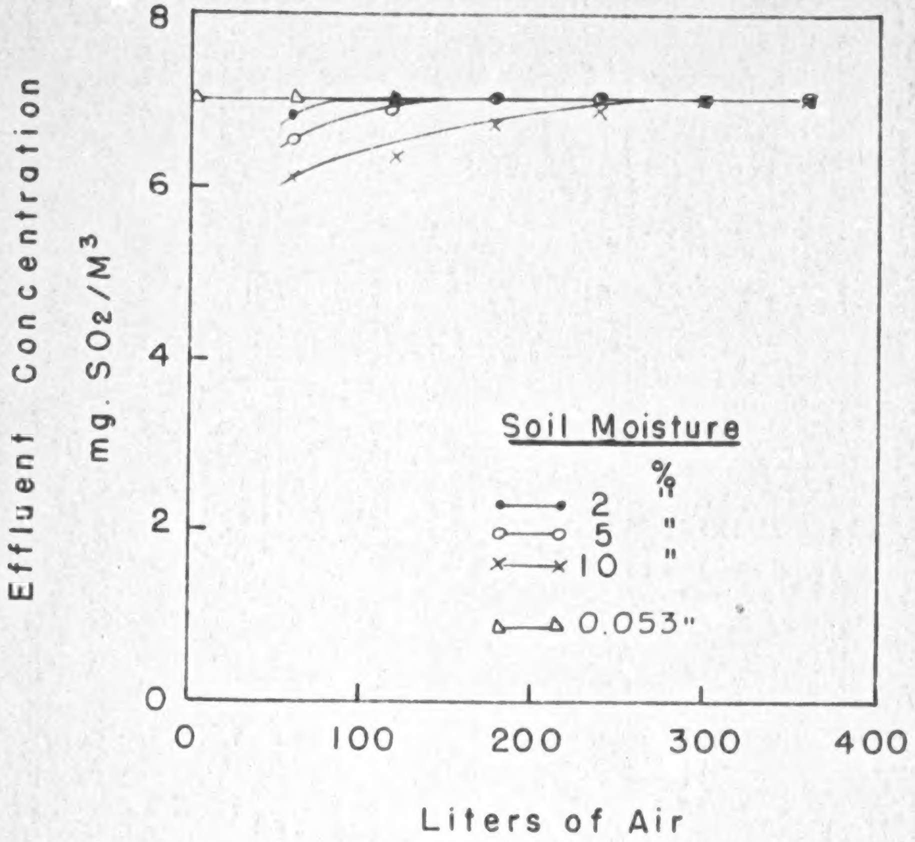

FIGURE 27 - ADSORPTION OF ATMOSPHERIC SULFUR DIOXIDE BY 13.3 sq. cm. OF LAKEWOOD SOIL.

TOTAL SOIL 10 GRAMS

INFLUENT CONCENTRATION 7.05 mg. $SO_2/M^3$.

## TABLE XXI

## AMOUNT OF SULFUR DIOXIDE REMOVED FROM AN AIR STREAM BY 13.3 SQ. CM. OF SOIL (25°C.)

| Micrograms $SO_2$ Applied | Soil Moisture (%) | Micrograms Removed | |
|---|---|---|---|
| | | Nixon Soil | Lakewood Soil |
| 4116 | 0.52 | 257 | - |
| 4116 | 2.0 | 270 | - |
| 4116 | 5.0 | 373 | - |
| 4116 | 10.0 | 598 | - |
| 2538 | 0.053 | - | - |
| 2538 | 2.0 | - | 13 |
| 2538 | 5.0 | - | 33 |
| 2538 | 10.0 | - | 115 |

### TABLE XXII

### COMPARISON OF SURFACE ABSORPTION OF WATER MIXED WITH SOIL AND SOME WATER SOLUTIONS

| Water Solution | ml. of Water | Air Concentration (mg. $SO_2/M^3$) | Total $SO_2$ Absorbed (micrograms) |
|---|---|---|---|
| Mixed with ten grams of Nixon soil | 1.11 | 6.87 | 341 |
| Distilled water | 1.11 | 6.87 | 15.9 |
| 3% NaCl | 1.11 | 6.87 | 15.2 |
| Sea water | 1.11 | 6.87 | 45.4 |
| 130 ppm. $NaHCO_3$ | 1.11 | 6.87 | 75.5 |
| Mixed with ten grams of Lakewood soil | 1.11 | 7.05 | 115 |
| Distilled water | 1.11 | 7.05 | 16.2 |
| 3% NaCl | 1.11 | 7.05 | 15.7 |
| Sea water | 1.11 | 7.05 | 46.7 |
| 130 ppm. $NaHCO_3$ | 1.11 | 7.05 | 76.8 |

that was dissolved in 1.11 ml. of distilled water from 15.9 to 341 micrograms, when an atmosphere of 6.87 mg. $SO_2/M^3$ was passed over the soil. Ten grams of Lakewood soil increased the solubility from 16.2 to 115 micrograms in 1.11 ml. of distilled water, when an atmosphere of 7.05 mg. $SO_2/M^3$ was passed over the soil.

### 4. Discussion

It is apparent from these studies that sulfur dioxide is adsorbed by a soil and this can contribute to the soil acidity. It has been shown that soil moisture has a significant influence on the amount of sulfur dioxide adsorbed by a soil so that in the case of acid soils of the Lakewood type no adsorption takes place in the absence of soil moisture.

The presence of soils with water greatly increased the amount of atmospheric sulfur dioxide that was dissolved by the water.

The adsorption of sulfur dioxide by soils varied with the pH of the original soil and the quantity of moisture present in the soil.

## C. Reactions of Sulfur Dioxide with Protein Solutions

### 1. General.

The solubility and reaction of atmospheric sulfur dioxide with biological fluids has been the subject of a great deal of speculation (5, 6, 34, 55, 57, 60, 72, 76). The important fluids are the blood and mucous. Air laden with sulfur dioxide passes through the respiratory tract and into the lung. In the respiratory tract the air passes over the mucous lining where solution of any atmospheric sulfur dioxide could take place. In the lungs, materials in the air are passed to the blood and transported throughout the body. The influence of dissolved sulfur dioxide on the proteins of these two fluids was studied.

The four proteins selected were albumin, fibrinogen, globulin, and hemoglobin. Water solutions of the four proteins were prepared and exposed in the test chamber to various concentrations of atmospheric sulfur dioxide. Sodium bicarbonate and potassium phosphate were added to the protein solutions and the solubility determined for these treated samples. Portions of the protein and treated protein solutions were titrated with dilute sulfuric and sulfurous acid.

Some of the properties of the proteins used in the study are given in Table XXIII. The values were obtained from several authors (27, 36, 37, 77). The proteins used in the study were egg albumin, bovine fibrinogen, bovine alpha-globulin, and bovine hemoglobin. While the total globulin reported in Table XXIII was 2 gm./100 ml., the alpha fraction found in the plasma is reported to be 0.1 to 0.2 gm./100 ml. (36). It was decided to prepared protein solutions in this range of concentrations and to use the same concentration for all of the proteins so that a comparison between each could be made. In addition, a 50 ppm. hemoglobin solution was prepared and exposed in the test chamber.

## 2. Procedures.

The albumin and globulin solutions were prepared in exactly the same manner, with the exception of the solvent. Albumin was suspended in distilled water and the globulin in 0.07 percent sodium chloride. Both solutions were mixed for several hours. The mixtures were filtered through glass wool, centrifuged, and then filtered through a millipore filter. The amount of protein in solution was estimated by measurement of the total nitrogen by the Kjeldahl method. The protein solutions were diluted with distilled or sodium chloride solution so that final concentration of protein in solution was 0.159 percent.

Fibrinogen and hemoglobin solutions were prepared by direct solution of the dry proteins. Fibrinogen was soluble in three percent sodium chloride, while hemoglobin was soluble in distilled water. Solutions containing 0.159 percent of these two proteins were prepared as well as a 50 ppm. solution of hemoglobin.

In addition to the water solutions of protein already mentioned, bicarbonate and phosphate buffers were added to the solutions and exposed in the test chamber. Sodium bicarbonate was added to the protein solutions in concentrations of 50 and 130 ppm. Sufficient $K_2HPO_4$ and $KH_2PO_4$ was added to the protein solutions so that each was $3 \times 10^{-4}M$ in the final solution.

Preliminary exposure of albumin, fibrinogen and globulin solutions to atmospheric sulfur dioxide resulted in a denaturation of the protein as evidenced by a coagulation of the protein. The presence of turbidity prevented the use of the colorimetric method for the determination of dissolved sulfur dioxide, therefore the iodimetric method was used to measure the sulfite in solution. In the case of the hemoglobin, the intense color of the water solutions prevented the use of the colorimetric method for dissolved sulfite determination, but it was found that diluted samples could be analyzed by the iodimetric method. Therefore the iodimetric method was used to measure the dissolved sulfur dioxide in all of the protein solutions.

## TABLE XXIII

## PROPERTIES OF PROTEINS

| | Albumin | Fibrinogen | Globulin | Hemoglobin |
|---|---|---|---|---|
| Approximate concentration | | | | |
| in plasma (gm./100 ml.) | 3-5 | 0.3-0.6 | 2 | - |
| in whole blood (gm./100 ml.) | - | - | - | 15 |
| Approximate molecular weight | 69,000 | 400,000 | 155,000-165,000 | 66,000 |
| Isoelectric point | 4.6-5.4 | 5.4 | 5.1-5.3 | 6.9 |

Preliminary tests exposing hemoglobin solutions to atmospheric sulfur dioxide resulted in a reduction in the color of the solutions and indicated a transformation of the native protein upon exposure to the gas. Spectra (Figures 28 and 29) were obtained on the original solutions using a Beckman Model DB Spectrophotometer. Four cm. cells were used with the 550 ppm. hemoglobin solution and 1 cm. cell with the hemoglobin solutions containing 0.159 percent protein.

The peaks that can be distinguished in Figure 28 for the 50 ppm. hemoglobin solution are 270, 405, 499 and 625 millimicrons. Exposed 50 ppm. hemoglobin solutions showed a reduction in the 405 millimicron peak and indicated that absorbance at that wavelength could be used as a measure of transformation of the native protein.

The peaks that can be distinguished in Figure 29 for the 0.159 percent hemoglobin solution are 500, 580, and 625 millimicrons. The absorbance below 430 millimicrons was complete so that the peak at 405 millimicrons could not be used as a measure of the transformation of the protein.

Preliminary tests indicated that a calibration curve for hemoglobin solutions read at a wavelength of 625 millimicrons gave a straight line. Absorbance at 625 millimicrons, therefore, was used as a measure of the transformation of the 0.159 percent hemoglobin solutions exposed to atmospheric sulfur dioxide.

The pH of every protein solution exposed was determined immediately after removal from the test chamber.

Twenty ml. portions of the protein solutions were placed in the test chamber and exposed to various atmospheric concentrations of sulfur dioxide in the range of 0.6 to 9.0 mg. $SO_2/M^3$.

### 3. Results.

a) Rate of Solution.--The rate of solution of atmospheric sulfur dioxide in plain and buffered protein solutions is shown in Figures 30 to 44.

From Figure 30 it can be seen that albumin solutions exposed to an atmosphere containing 0.87 mg. $SO_2/M^3$ had not reached saturation after eight hours. With higher atmospheric concentrations the rate of solution is more rapid so that samples exposed to 7.55 mg. $SO_2/M^3$ reached saturation in about five hours.

While the buffered albumin solutions (Figures 31 and 32) show an increased rate of solution over the buffered solutions, the time required to reach saturation was relatively long -- four hours or more. From Figure 33 it can be seen that fibrinogen solutions exposed to 0.73 mg. $SO_2/M^3$ had not reached saturation after 7.5 hours, but when the atmospheric concentration was increased to 5.48 mg. $SO_2/M^3$ the protein solutions reached saturation

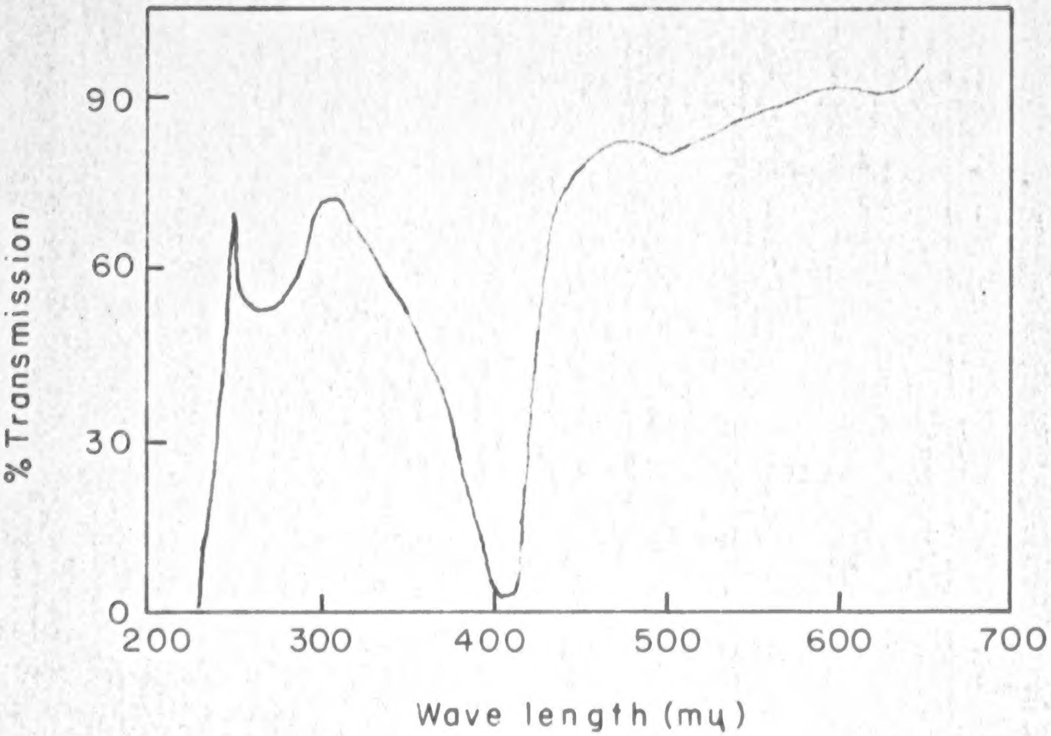

FIGURE 28 - SPECTRA OF A 50 ppm HEMOGLOBIN SOLUTION

4 cm. LIGHT PATH

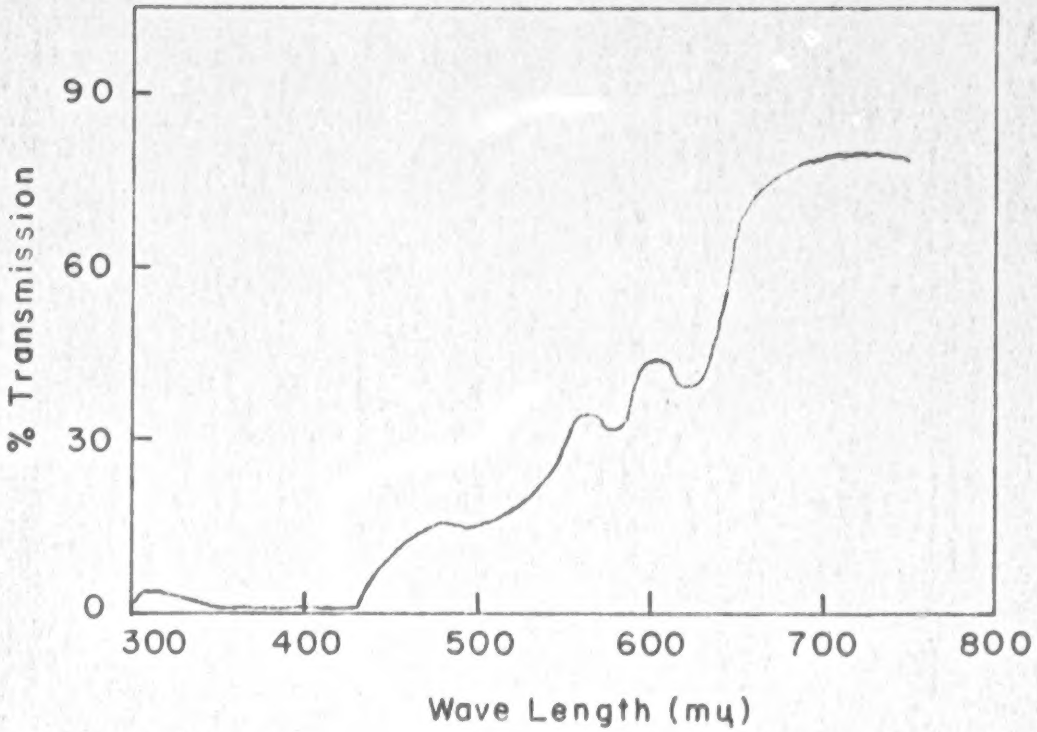

FIGURE 29 - SPECTRA OF A 0.159% HEMOGLOBIN SOLUTION

1 cm. LIGHT PATH

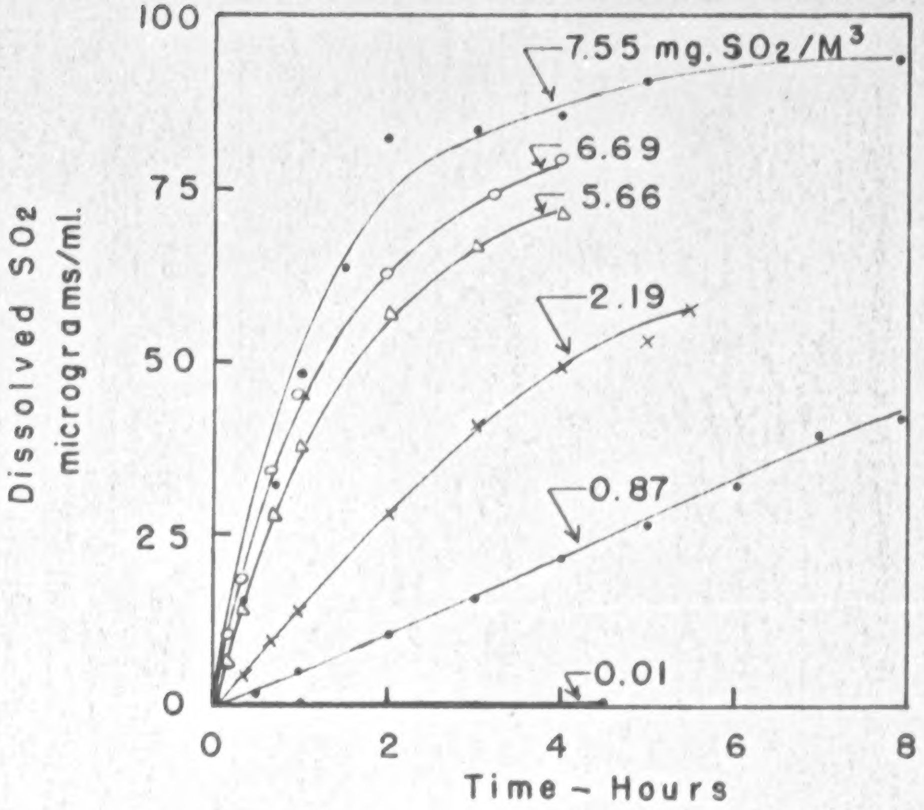

FIGURE 30 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN A 0.159% ALBUMIN SOLUTION

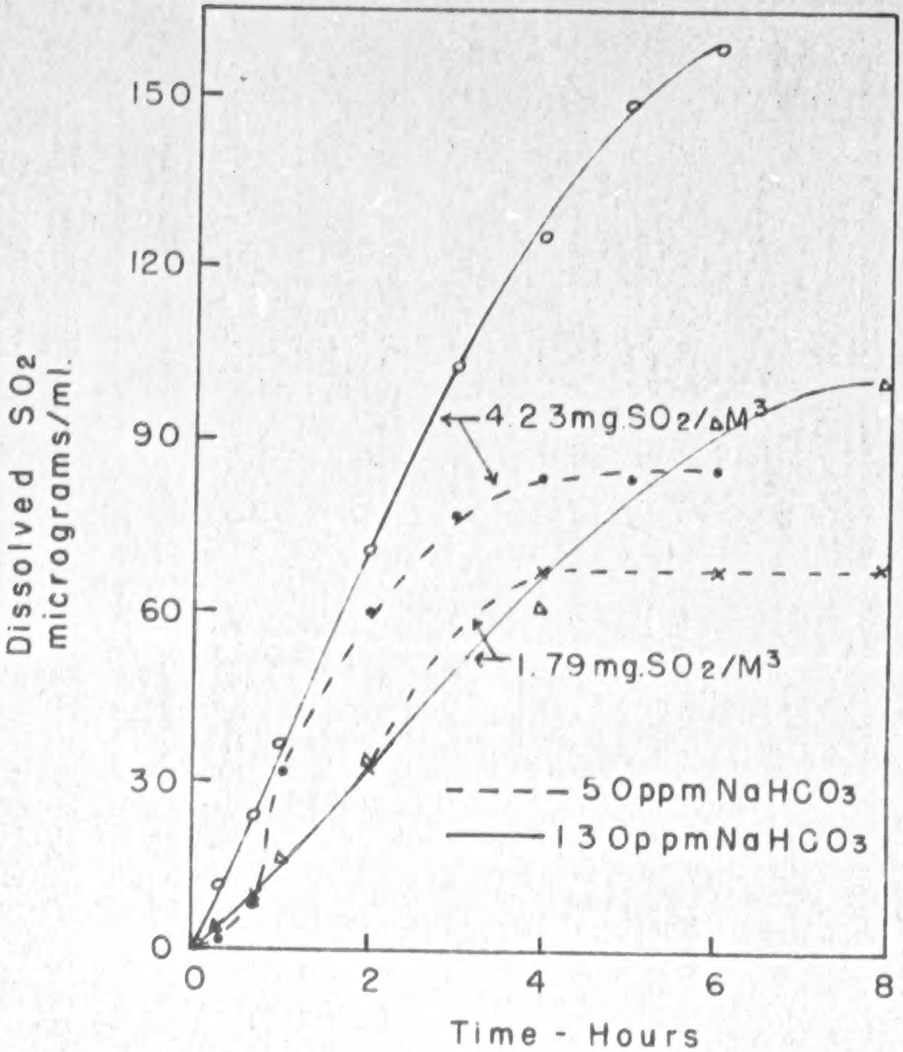

FIGURE 31 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN BICARBONATE BUFFERED 0.159% EGG ALBUMIN SOLUTION

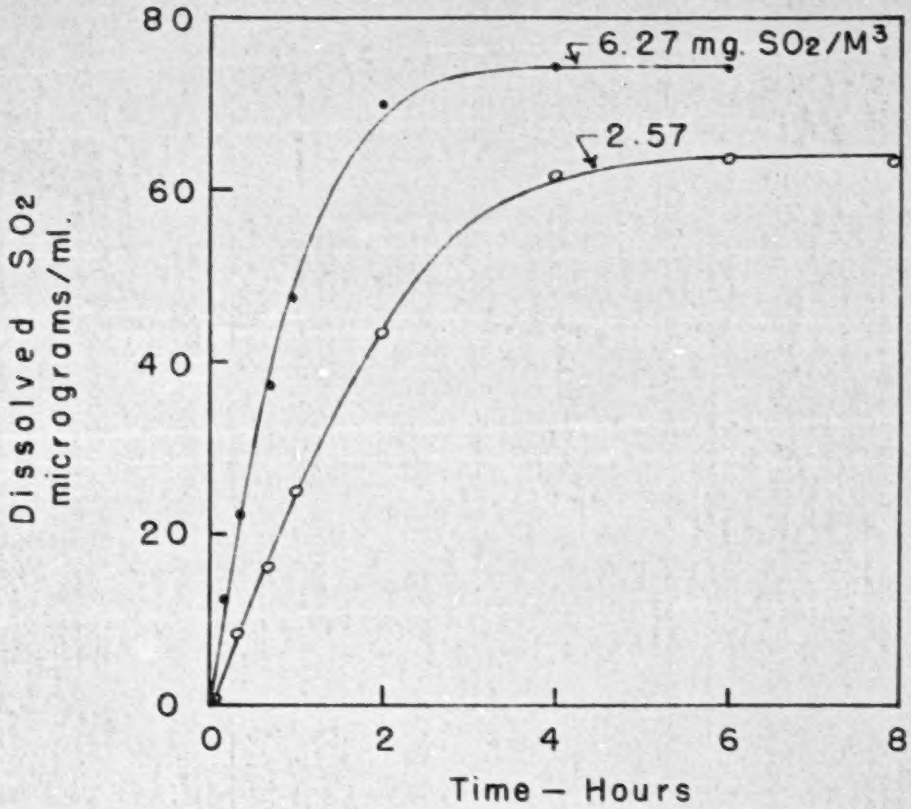

FIGURE 32 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE

IN PHOSPHATE BUFFERED 0.159% EGG ALBUMIN SOLUTION

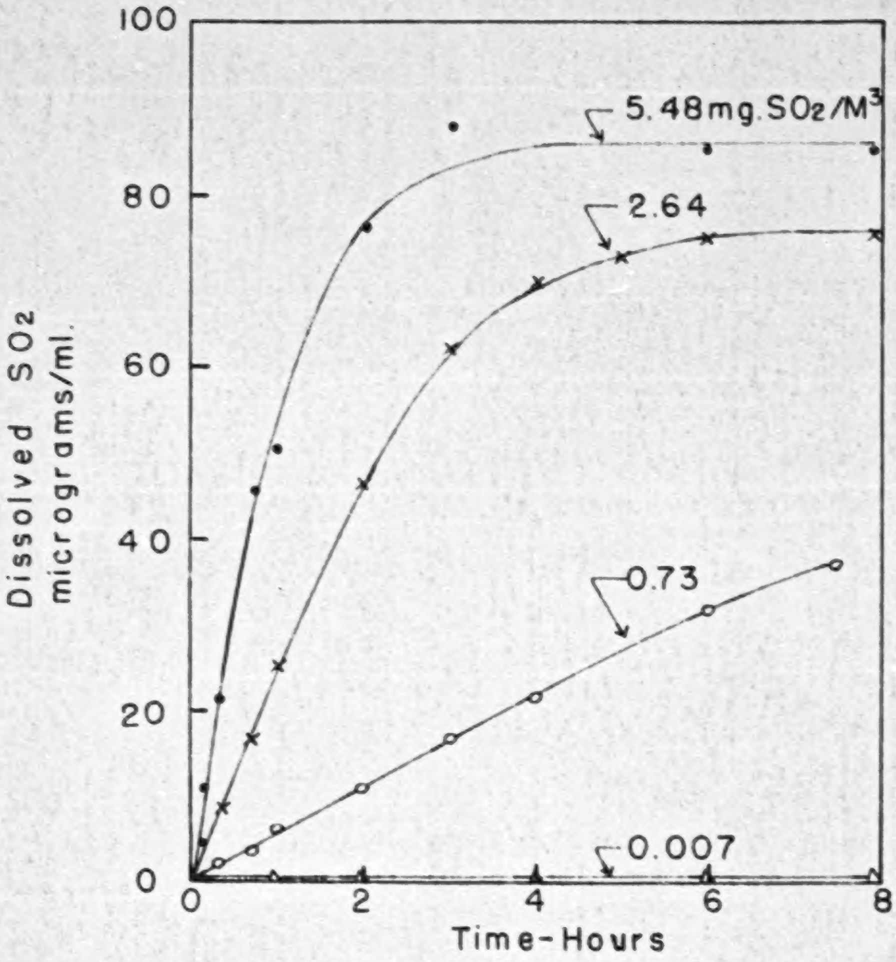

FIGURE 33 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN A 0.159% FIBRINOGEN SOLUTION IN 3% SODIUM CHLORIDE

in four hours. The presence of the bicarbonate and phosphate buffers increased the solubility of atmospheric sulfur dioxide (Figures 34 and 35), but the time required to reach saturation values, except at the higher concentrations, was in excess of four hours.

It can be seen from Figure 36 that globulin solutions exposed to 0.68 mg. $SO_2/M^3$ took four hours to reach saturation, while at 6.97 mg. $SO_2/M^3$ the solutions reached saturation in three hours. The presence of buffers increased the solubility of atmospheric sulfur dioxide (Figures 37 and 38) in globulin solutions, but the time required to reach saturation, except at the higher atmospheric concentrations, was in excess of four hours.

Figure 39 shows the rate of absorption of atmospheric sulfur dioxide by 0.159 percent hemoglobin solutions. For the three atmospheric concentrations used, it took three hours to reach saturation. The buffered hemoglobin solutions (Figures 40 and 41) also took approximately three hours to reach saturation with the exception of the solution containing 130 ppm. of sodium bicarbonate and exposed to 2.75 mg. $SO_2/M^3$ which took almost six hours to reach saturation.

The rate of solution of atmospheric sulfur dioxide in 50 ppm. hemoglobin solutions is shown in Figures 42, 43 and 44. It can be seen from Figure 42 that the rate of solution of atmospheric sulfur dioxide in solutions containing 50 ppm. hemoglobin was rapid and reached saturation in two hours or less. This rate is very close to that of distilled water alone and was to be expected with the very dilute hemoglobin solutions used in this study. Even the samples exposed to 0.60 mg. $SO_2/M^3$ reached saturation in two hours.

Figures 43 and 44 show that the presence of the buffers increased the amount of dissolved sulfur dioxide at saturation, but there was no change in the time required for the samples to reach saturation.

Comparisons of the solubility of atmospheric sulfur dioxide in the various protein solutions, buffered and unbuffered, are shown in Figures 45 to 49 for samples exposed for four hours in the test chamber.

It may be concluded, in general, that the solubility of atmospheric sulfur dioxide in the protein solutions is much greater than that in distilled water, and the presence of even traces of a few parts per million of bicarbonate buffer increase the solubility of the gas in the protein solutions.

The pH value of the unbuffered protein solutions decreased rapidly upon exposure to atmospheric sulfur dioxide to a value near 4.5 and remained at that level with continued exposure. The pH of the 50 ppm. hemoglobin solution decreased even further to a value of 4.0. The presence of bicarbonate and phosphate buffers delayed the decrease in the pH so that it did not drop as rapidly, but the final value was about 4.5 after several hours of exposure.

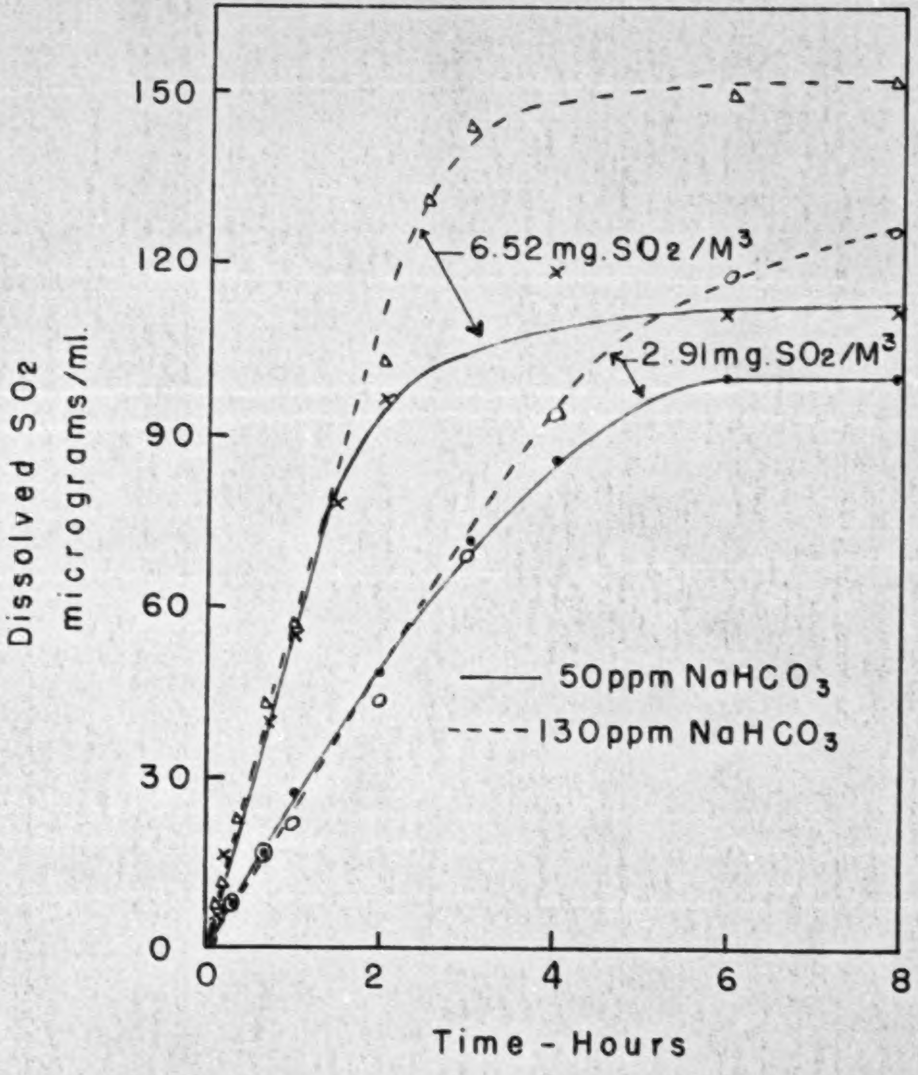

FIGURE 34 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN BICARBONATE BUFFERED 0.159% FIBRINOGEN SOLUTION IN 3% NaCl

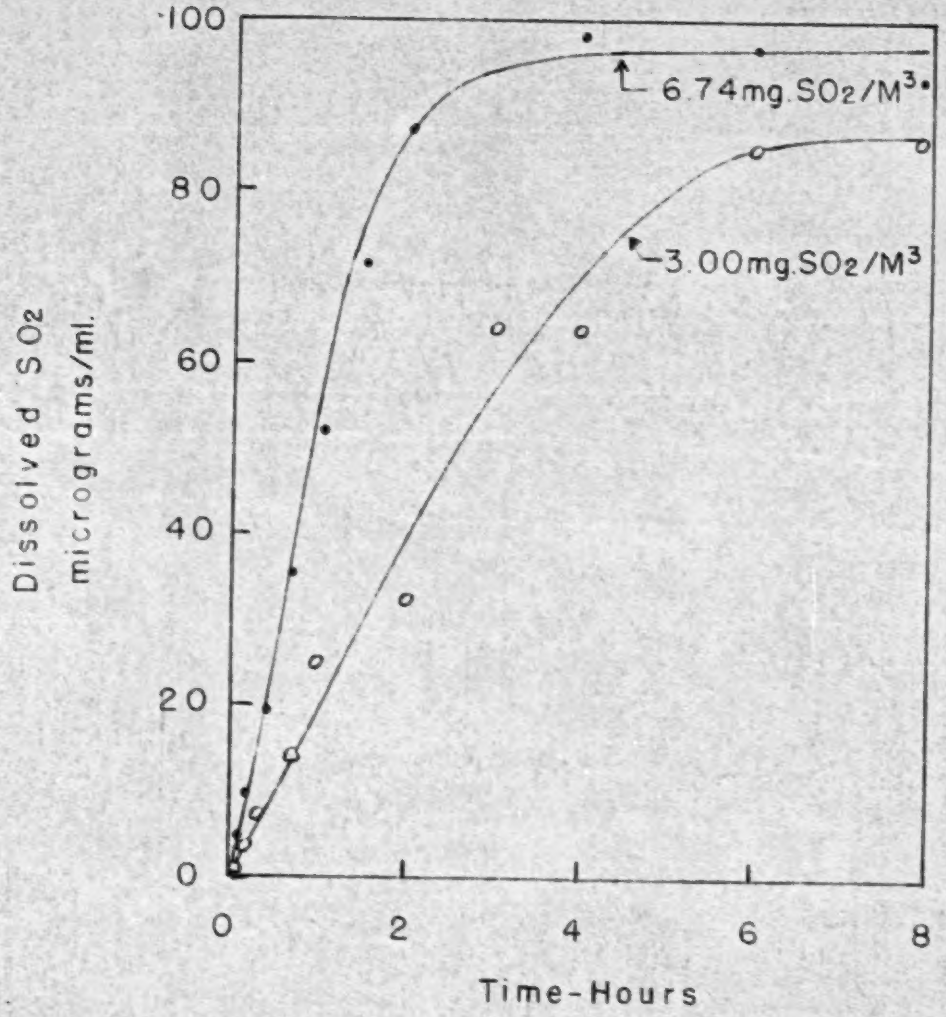

FIGURE 35 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE

IN PHOSPHATE BUFFERED 0.159% FIBRINOGEN SOLUTION

IN 3% NaCl

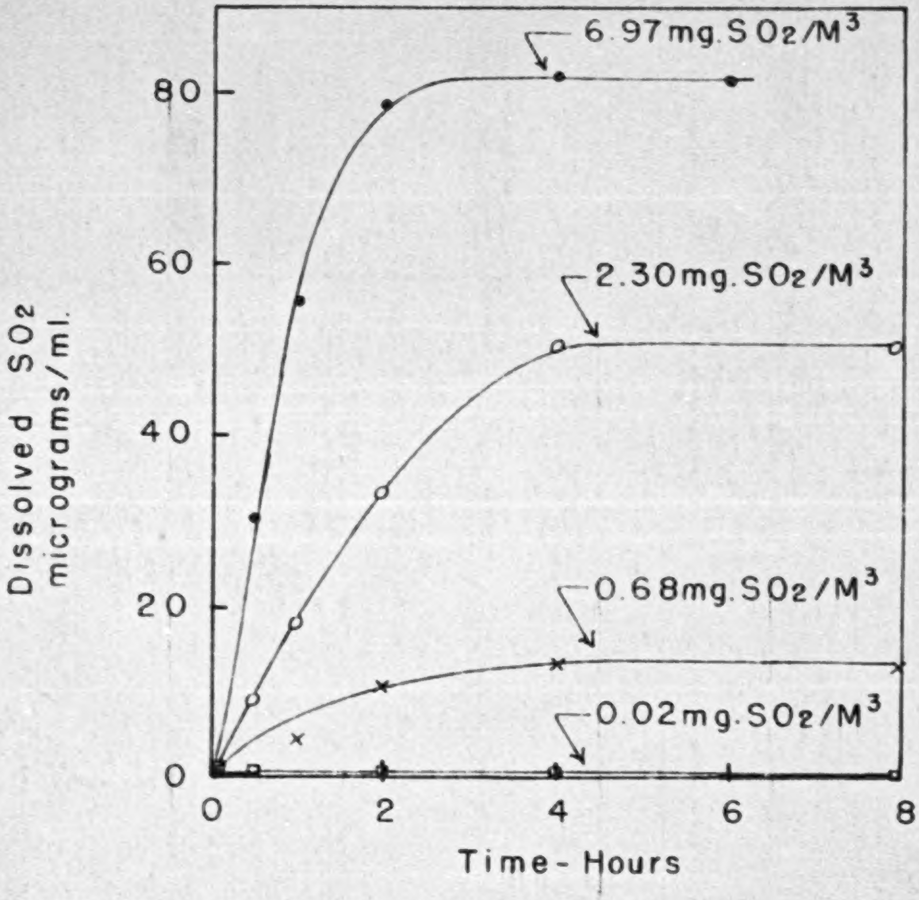

FIGURE 36 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN 0.159% GLOBULIN SOLUTION

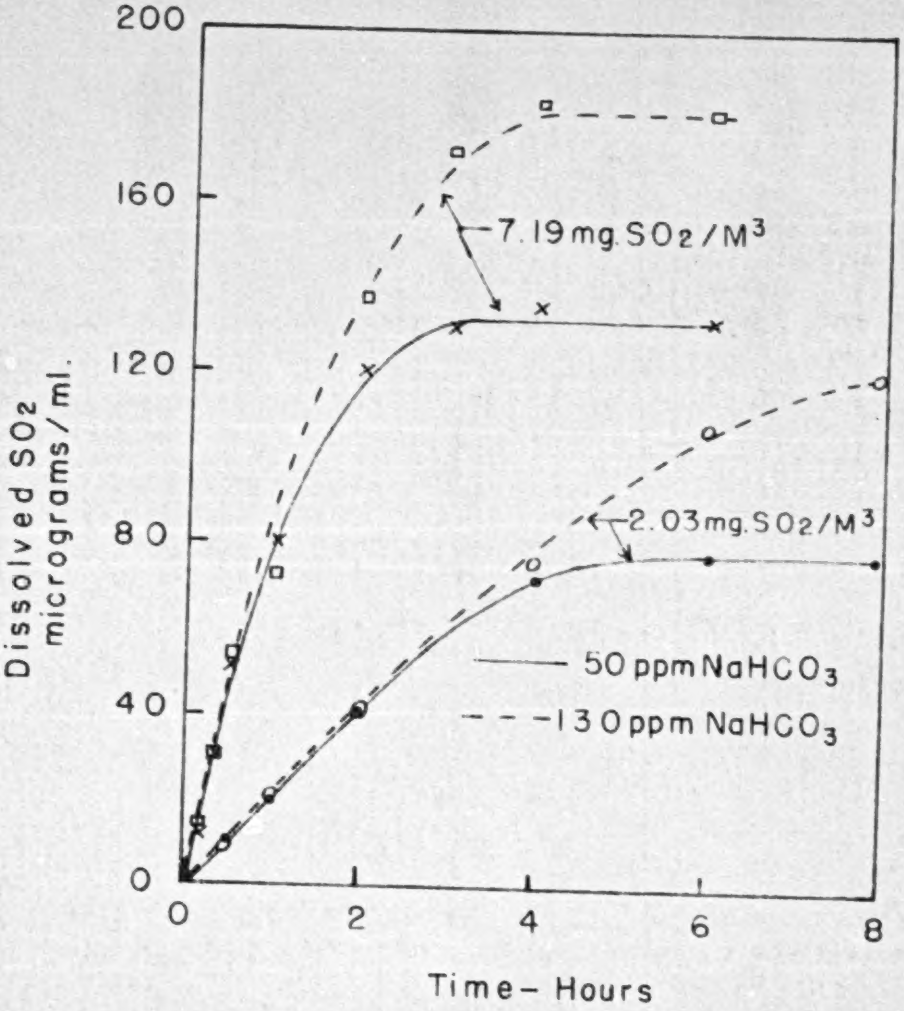

FIGURE 37 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN BICARBONATE BUFFERED 0.159% GLOBULIN SOLUTION

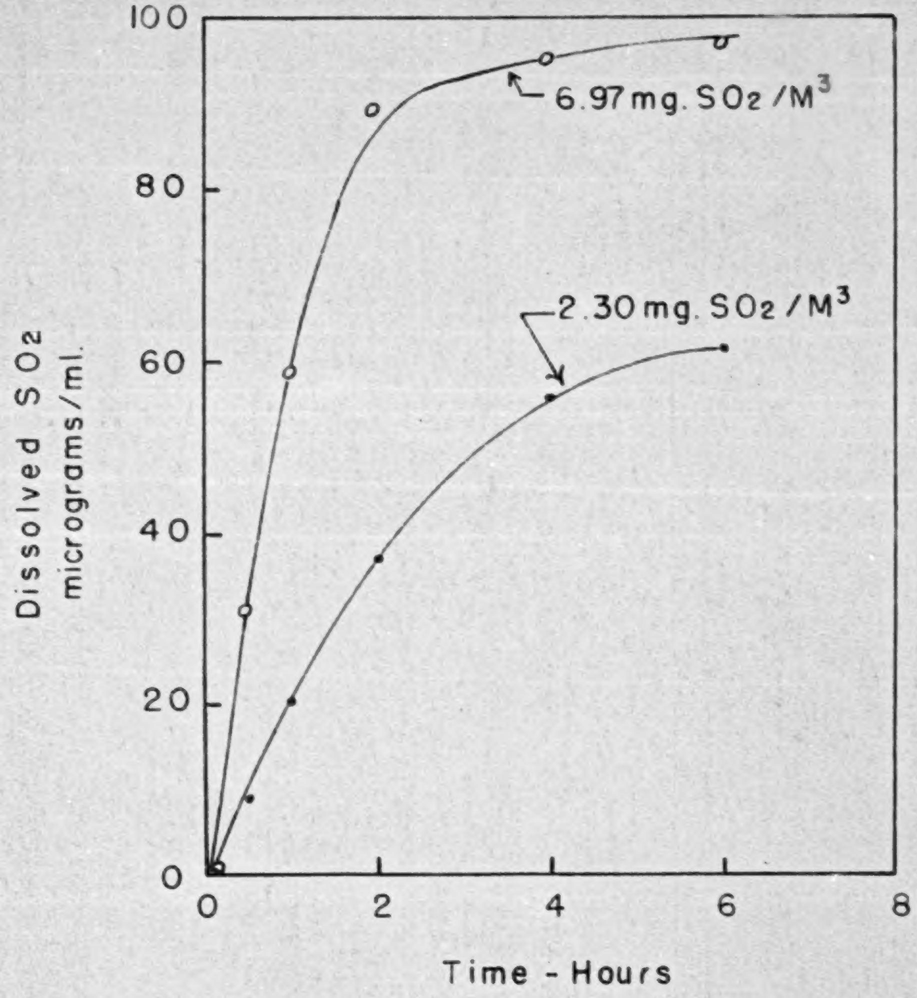

FIGURE 38 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN PHOSPHATE BUFFERED 0.159% GLOBULIN SOLUTION

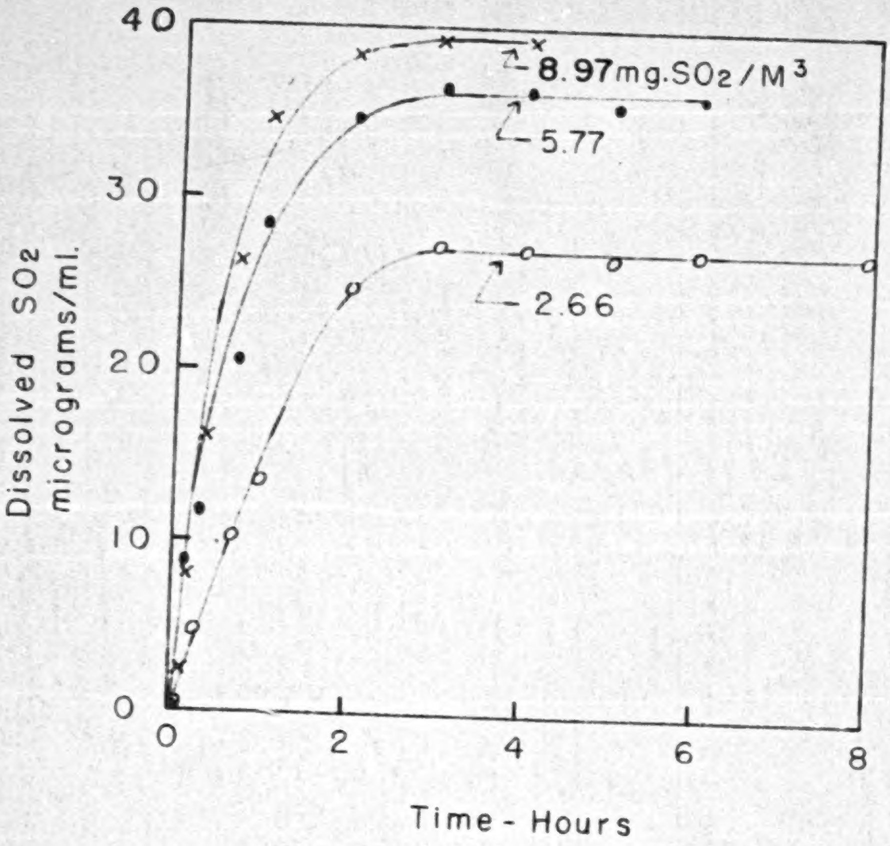

FIGURE 39 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN 0.159% HEMOGLOBIN SOLUTION

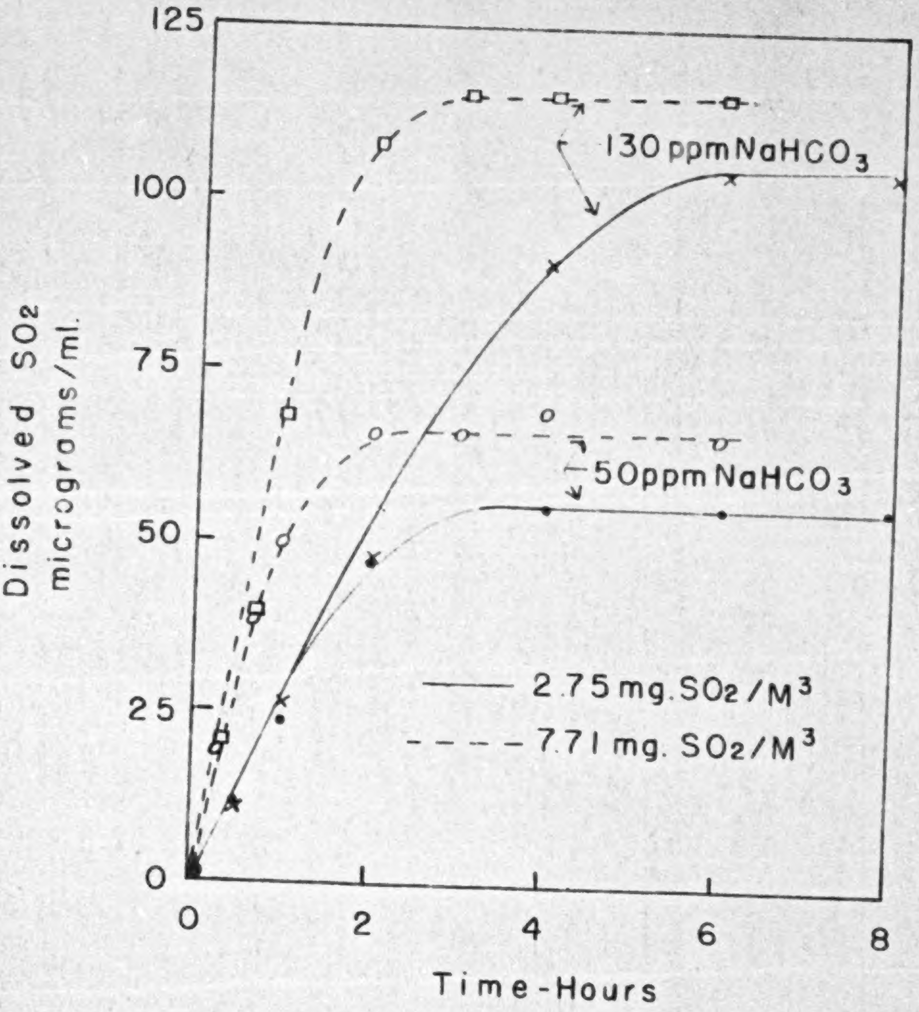

FIGURE 40 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN BICARBONATE BUFFERED 0.159% HEMOGLOBIN SOLUTION

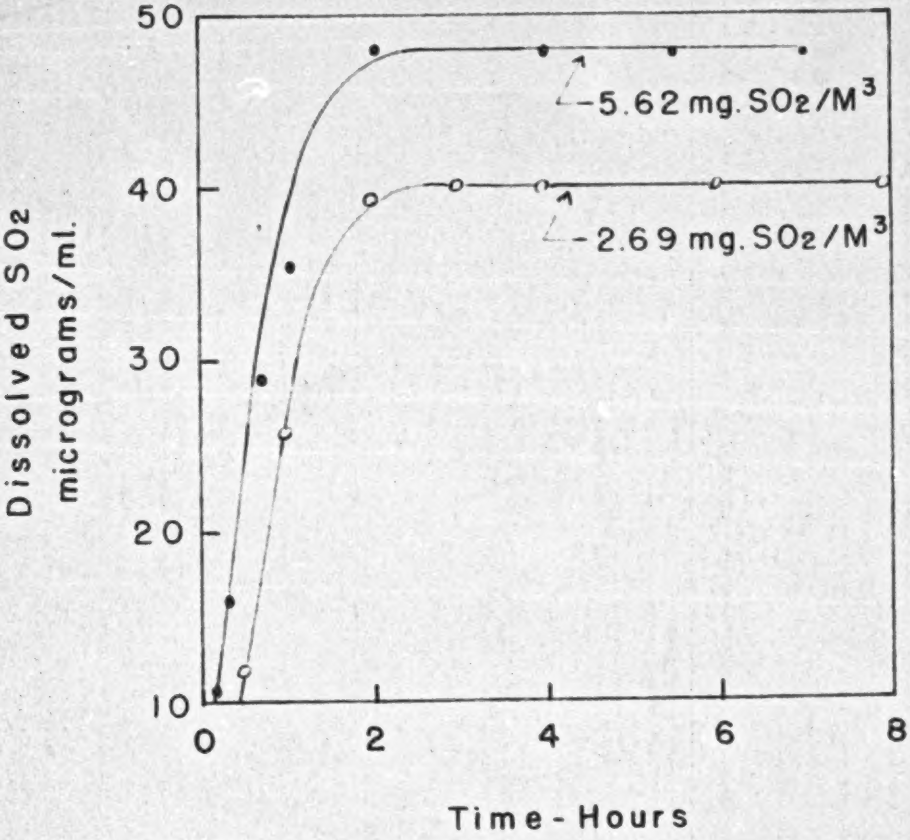

FIGURE 41 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN PHOSPHATE BUFFERED 0.159% HEMOGLOBIN SOLUTION

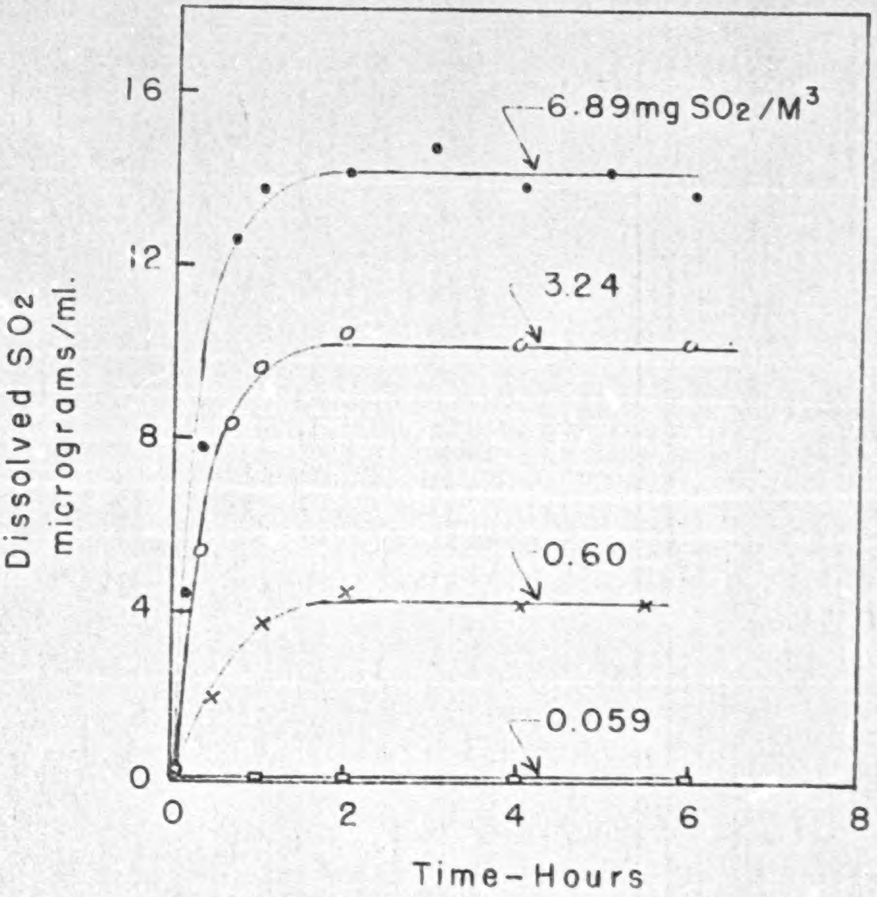

FIGURE 42 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN 50 ppm HEMOGLOBIN SOLUTION

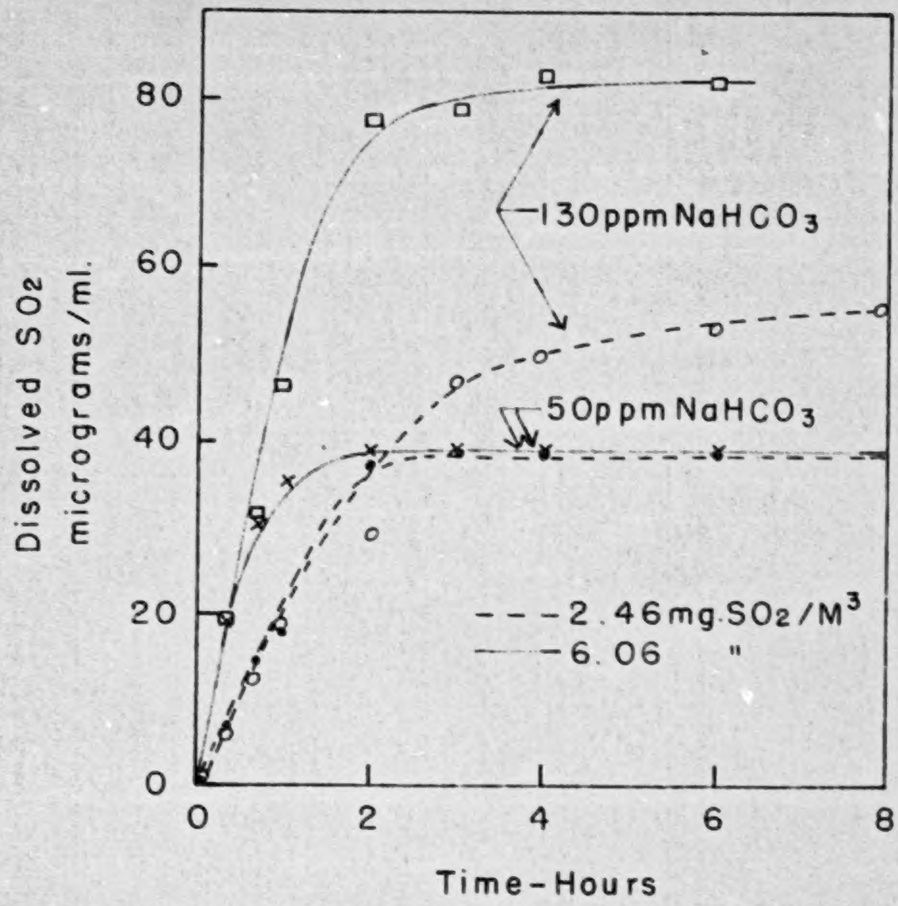

FIGURE 43 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN BICARBONATE BUFFERED 50 ppm HEMOGLOBIN SOLUTION

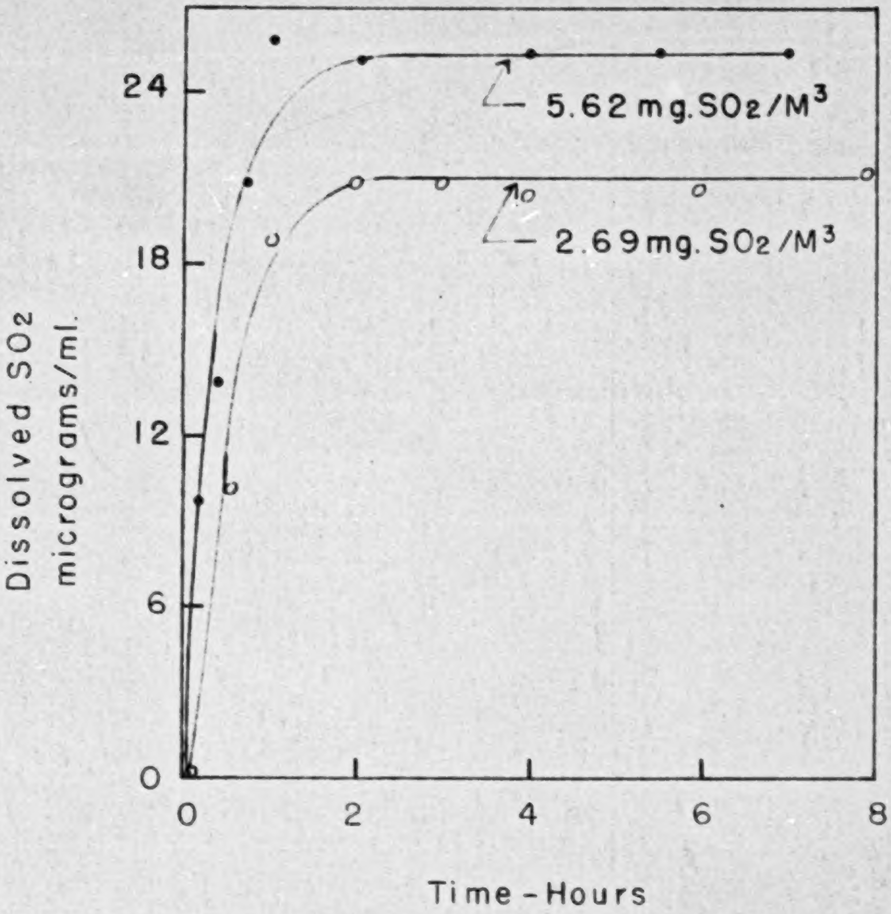

FIGURE 44 - RATE OF SOLUTION OF ATMOSPHERIC SULFUR DIOXIDE IN PHOSPHATE BUFFERED 50 ppm HEMOGLOBIN SOLUTION

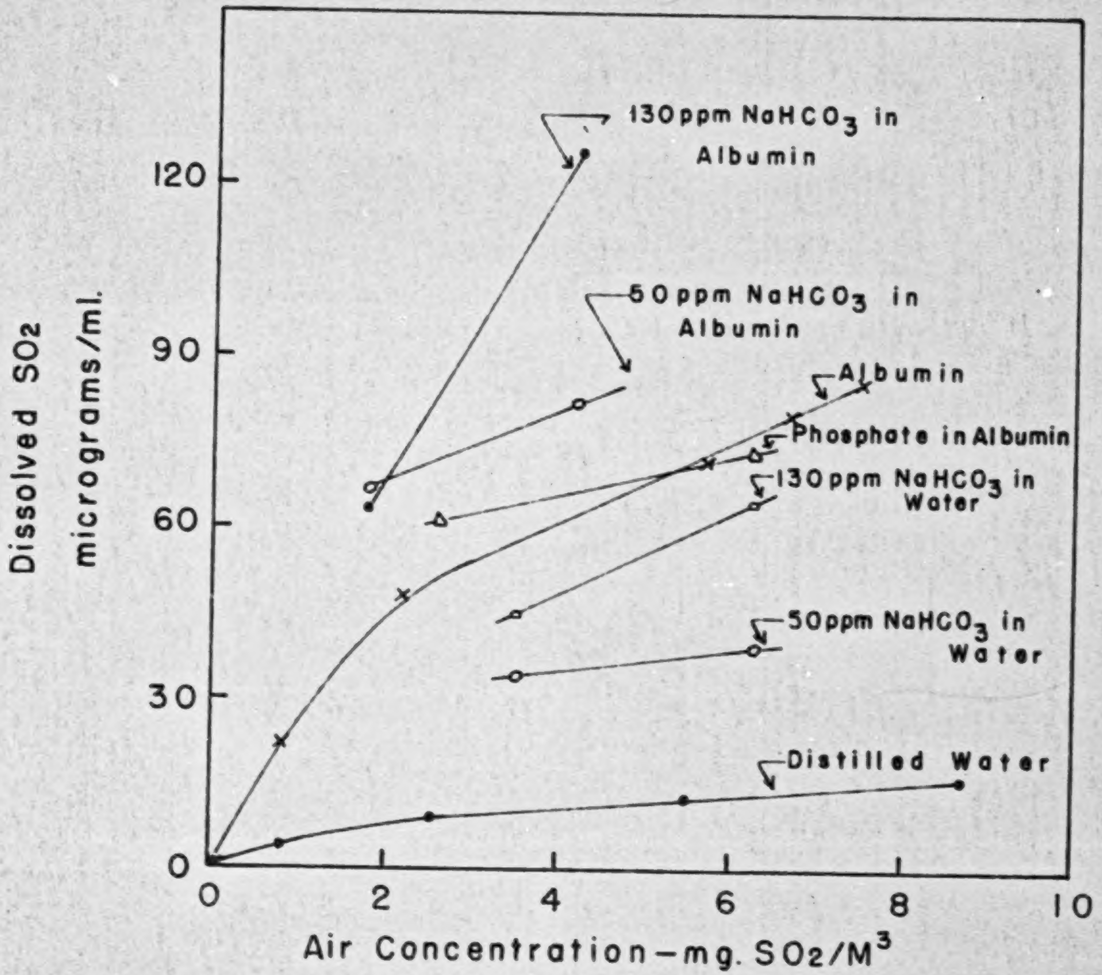

FIGURE 45 - SOLUBILITY OF ATMOSPHERIC SULFUR DIOXIDE IN ALBUMIN SOLUTION - EXPOSED FOUR HOURS

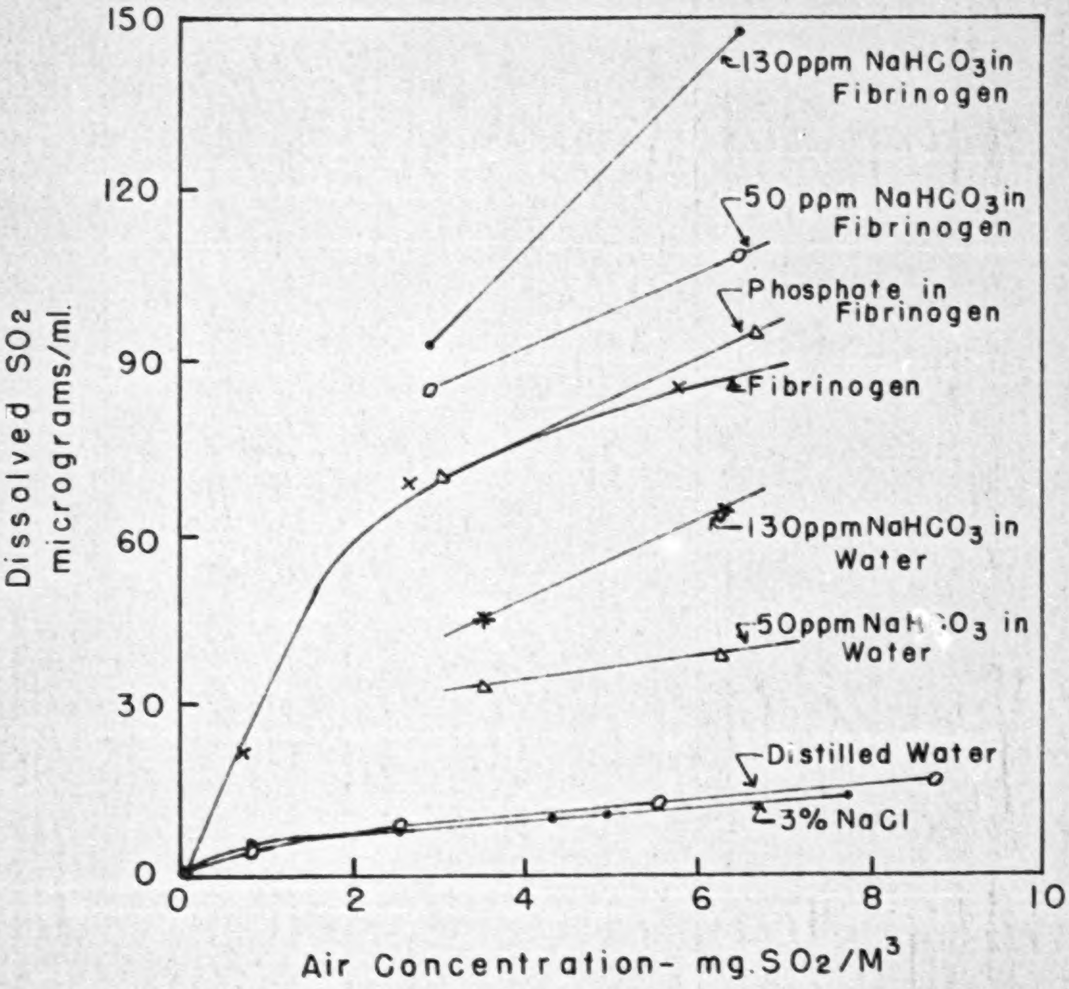

FIGURE 46 - SOLUBILITY OF ATMOSPHERIC SULFUR DIOXIDE IN 0.159% FIBRINOGEN SOLUTION - EXPOSED FOUR HOURS

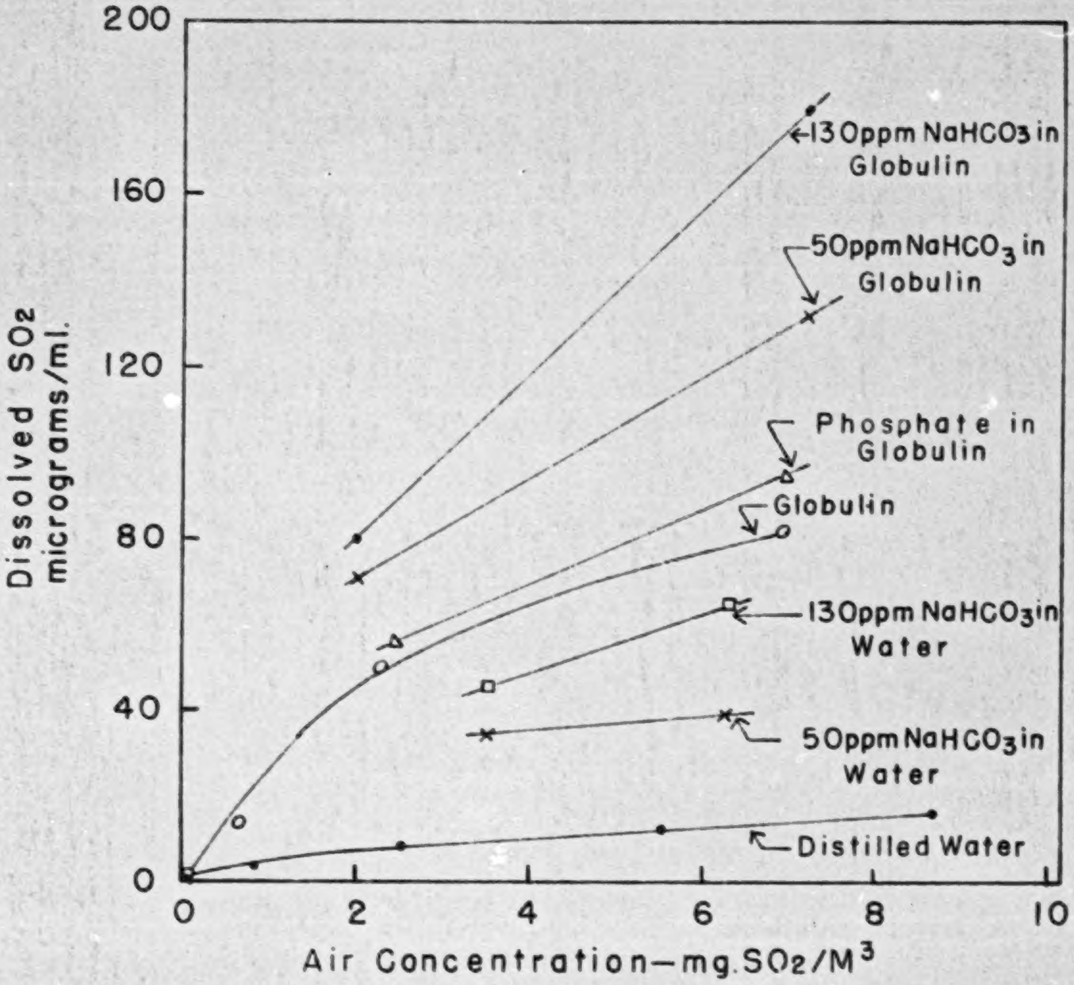

FIGURE 47 - SOLUBILITY OF ATMOSPHERIC SULFUR DIOXIDE IN 0.159% GLOBULIN SOLUTION - EXPOSED FOUR HOURS

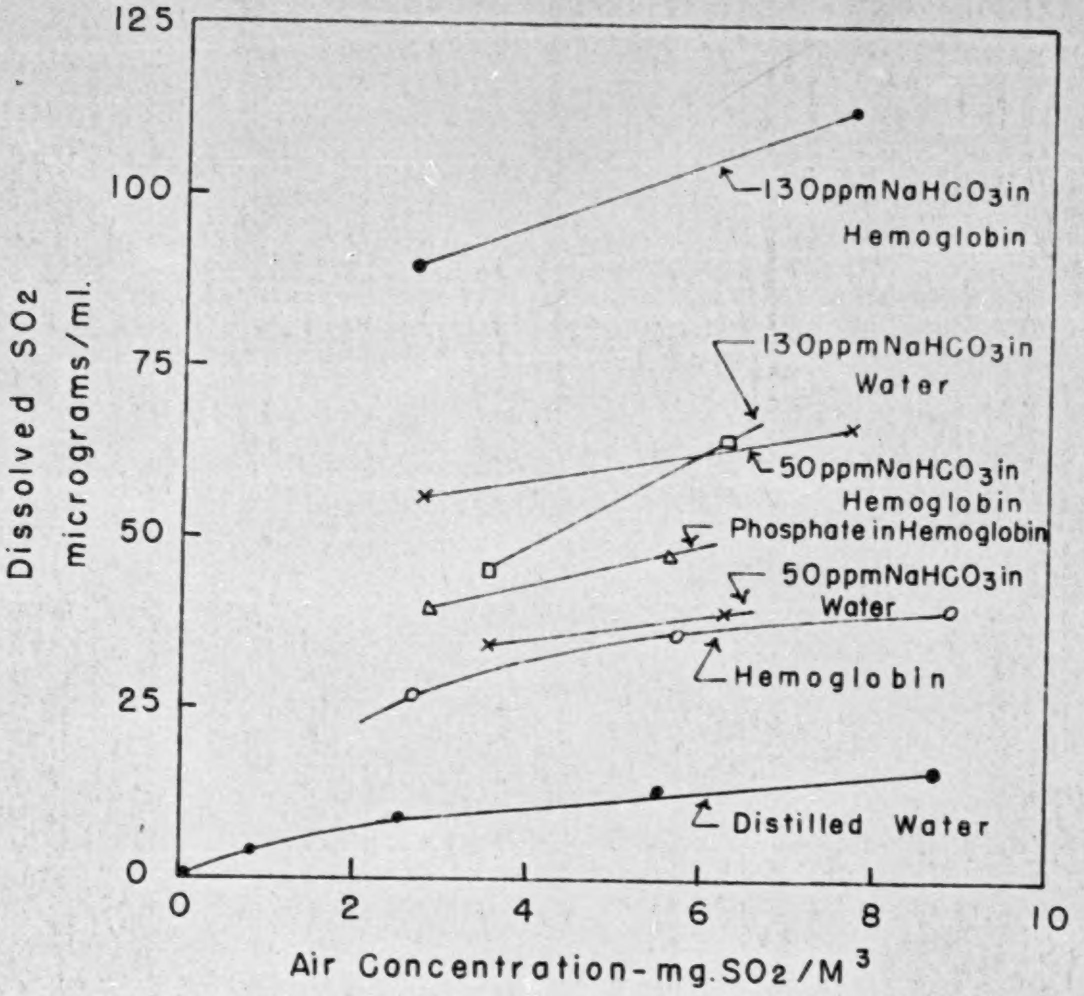

FIGURE 48 - SOLUBILITY OF ATMOSPHERIC SULFUR DIOXIDE IN 0.159% HEMOGLOBIN SOLUTION - EXPOSED FOUR HOURS

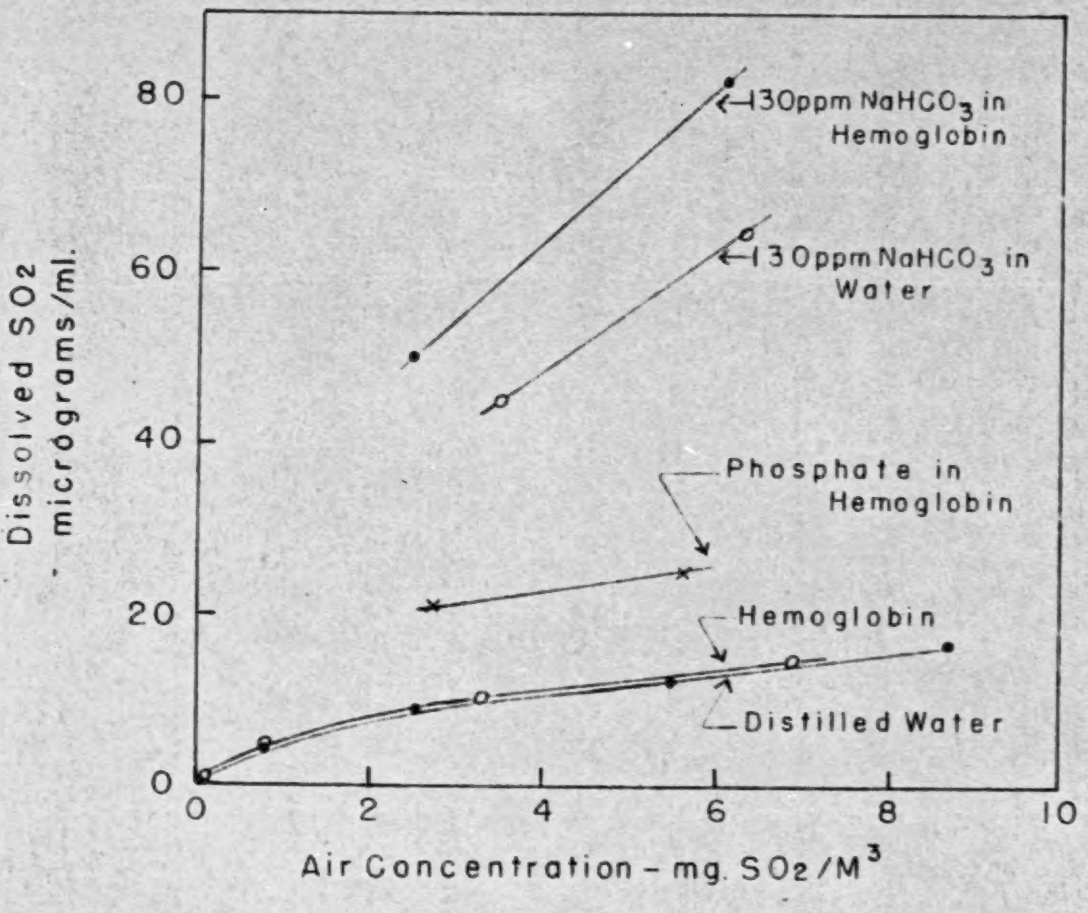

FIGURE 49 - SOLUBILITY OF ATMOSPHERIC SULFUR DIOXIDE IN 50 ppm HEMOGLOBIN SOLUTION - EXPOSED FOUR HOURS

b) Reaction of Protein.--It was observed that after a period of exposure to atmospheric sulfur dioxide the albumin, fibrinogen, and globulin started to coagulate, and the time for the start of coagulation was less with the higher atmospheric concentrations of the gas. Figures 50 and 51 show the variation in the turbidity, expressed as optical density, of 0.159 percent albumin and fibrinogen solutions at different levels of dissolved sulfur dioxide. It can be seen that the turbidity reaches a maximum when the sulfur dioxide concentration in the solution reaches 44 micrograms/ml. in the case of the albumin solutions. The turbidity of the fibrinogen solution reached a maximum when the dissolved sulfur dioxide was between 70 and 90 micrograms/ml. When the turbidity of the buffered solutions was checked against the amount of dissolved sulfur dioxide, it was found that it required more sulfur dioxide before the maximum turbidity was reached. In addition, the turbidity did not occur at exactly the same concentration for all of the buffered albumin and fibrinogen solutions but varied with the amount of buffer in the solution. Albumin solutions containing 50 ppm. of sodium bicarbonate had 60 micrograms $SO_2$/ ml. in solution when turbidity was at a maximum. With an increase in the sodium bicarbonate to 130 ppm. almost 160 micrograms $SO_2$/ml. was required before maximum turbidity was reached. Fibrinogen solutions had 100 micrograms $SO_2$/ml. in solution at maximum turbidity when 50 ppm. sodium bicarbonate was present and 135 micrograms $SO_2$/ml. with 130 ppm. of sodium bicarbonate.

The decrease in turbidity indicated in Figures 50 and 51 after prolonged exposure of the albumin and fibrinogen does not represent redissolving of the protein. Agglomeration of the fine precipitate into large particles which settled rapidly had the effect of apparently reducing the turbidity of the solution as more sulfur dioxide was dissolved.

In the case of globulin, no relationship was found between the level of the turbidity and the amount of dissolved sulfur dioxide, except that more sulfite was required in the buffered solutions before coagulation took place.

The reaction of sulfur dioxide with the hemoglobin was measured by the decrease in absorbance of the solution. No correlation was found between the levels of sulfur dioxide in solution and the amount of hemoglobin formation of the protein, whether coagulation or change in absorbance, do not give the time that it took for the reaction between the protein and the dissolved sulfur to occur. Figures 53 to 57 show the times required for the various protein solutions to react at different atmospheric concentrations of sulfur dioxide.

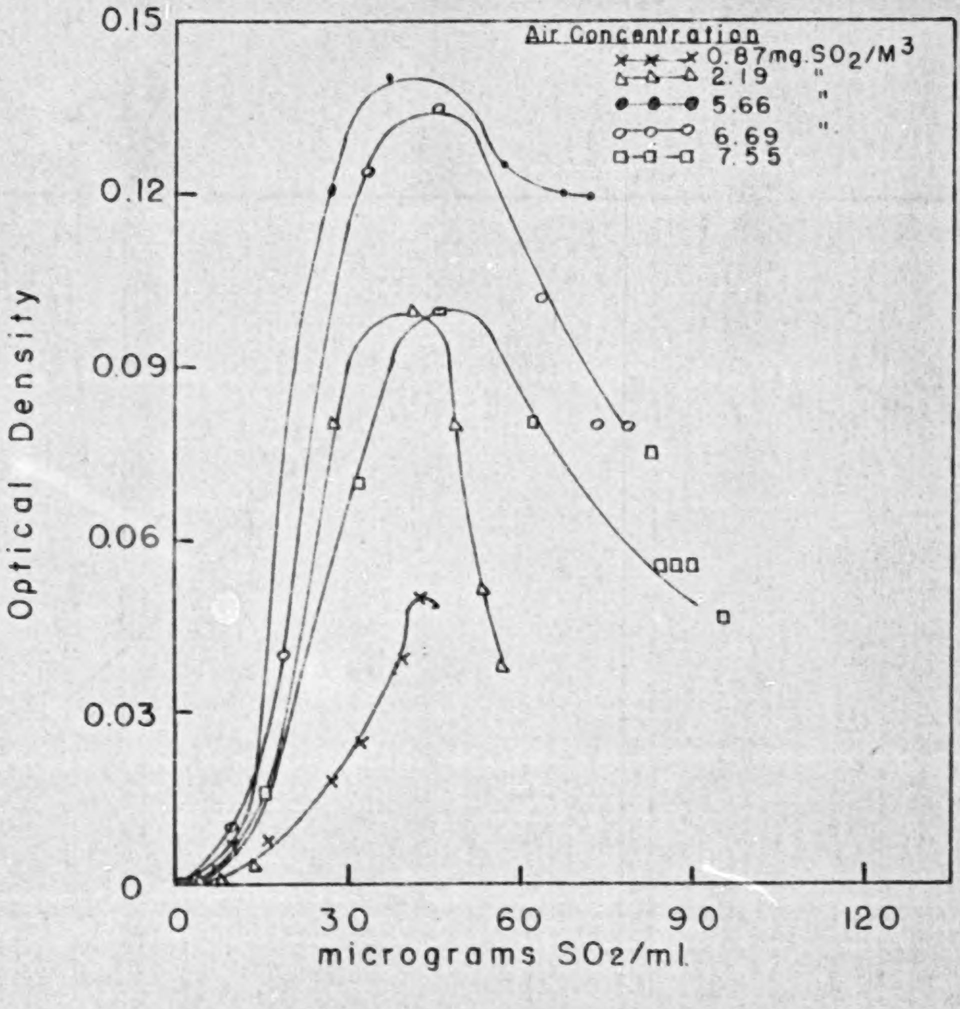

FIGURE 50 - VARIATION IN TURBIDITY OF A 0.159% EGG ALBUMIN SOLUTION AT DIFFERENT LEVELS OF DISSOLVED SULFUR DIOXIDE

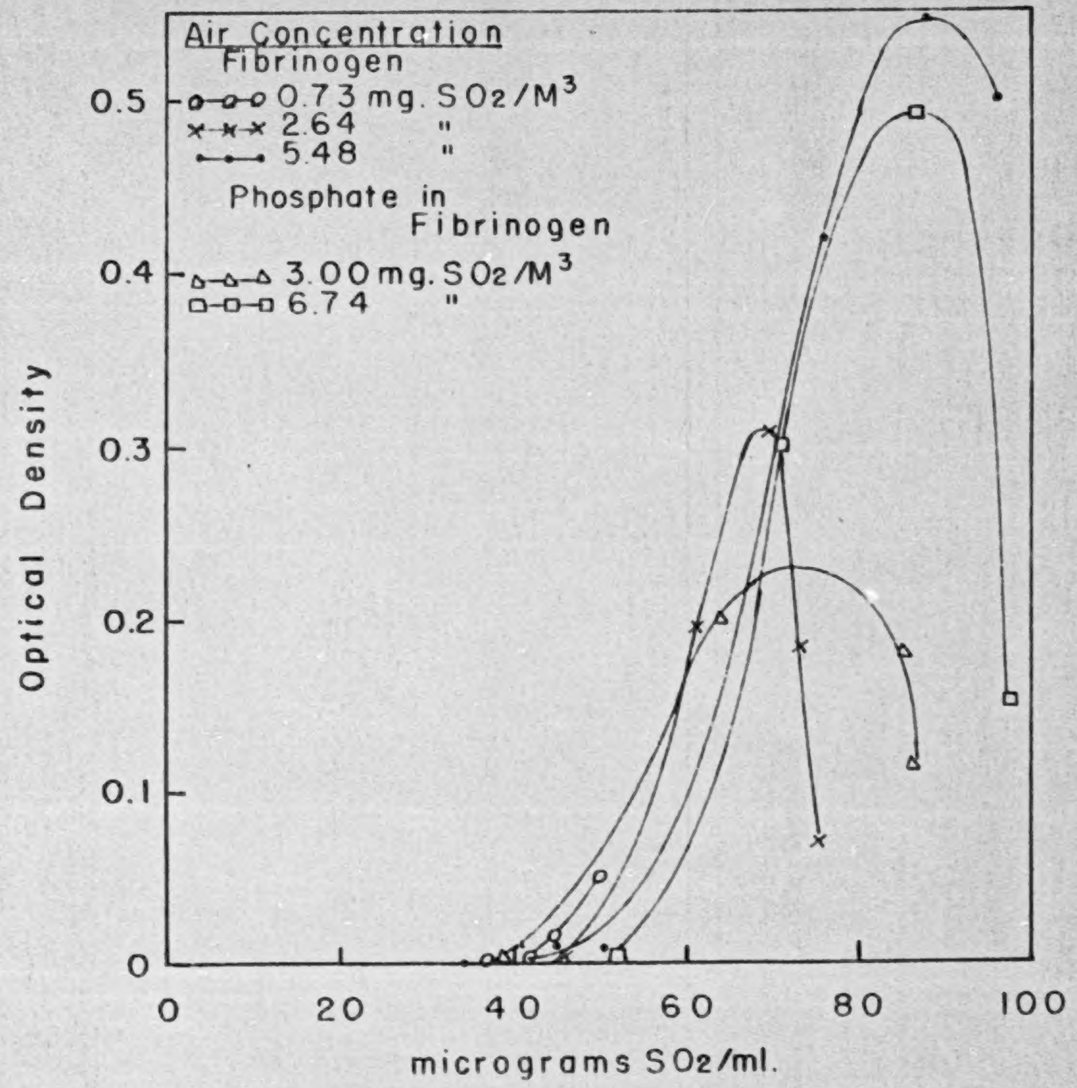

FIGURE 51 - VARIATION IN TURBIDITY OF A 0.159% FIBRINOGEN SOLUTION IN A 3% SODIUM CHLORIDE SOLUTION AT DIFFERENT LEVELS OF DISSOLVED SULFUR DIOXIDE

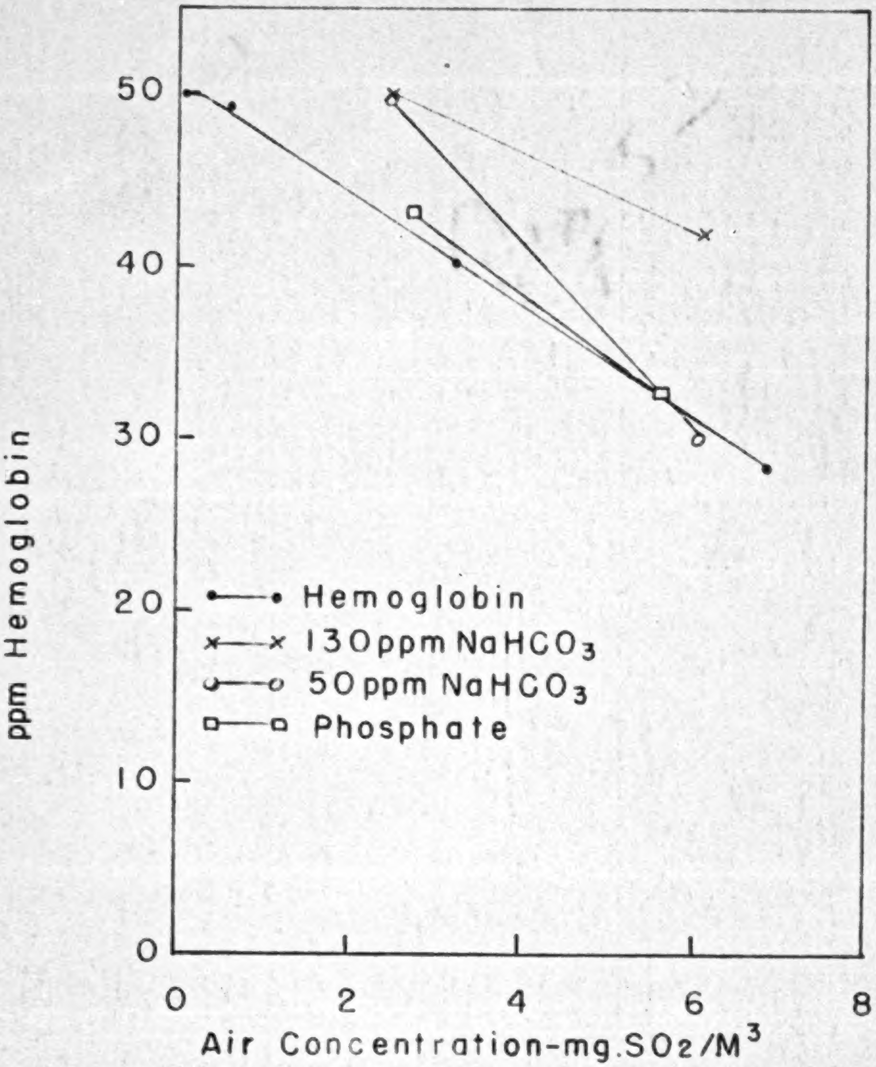

FIGURE 52 - HEMOGLOBIN REMAINING AFTER FOUR HOUR EXPOSURES TO ATMOSPHERIC SULFUR DIOXIDE

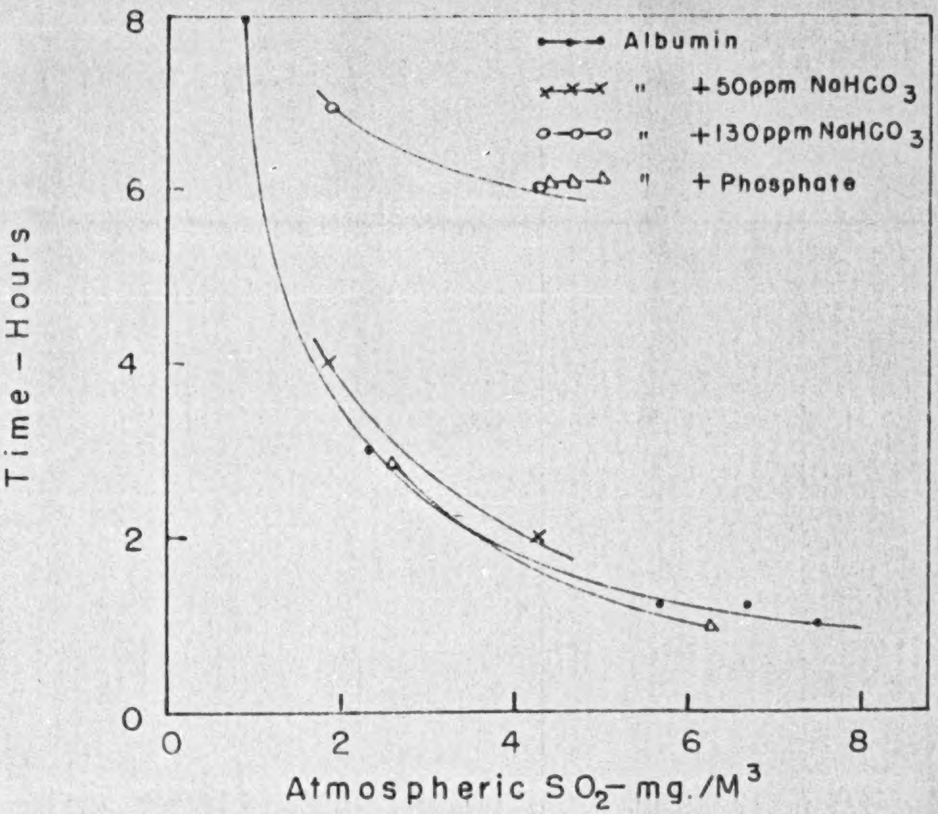

FIGURE 53 - TIME FOR 0.159% ALBUMIN SOLUTION TO REACH MAXIMUM TURBIDITY WHEN EXPOSED TO ATMOSPHERIC SULFUR DIOXIDE

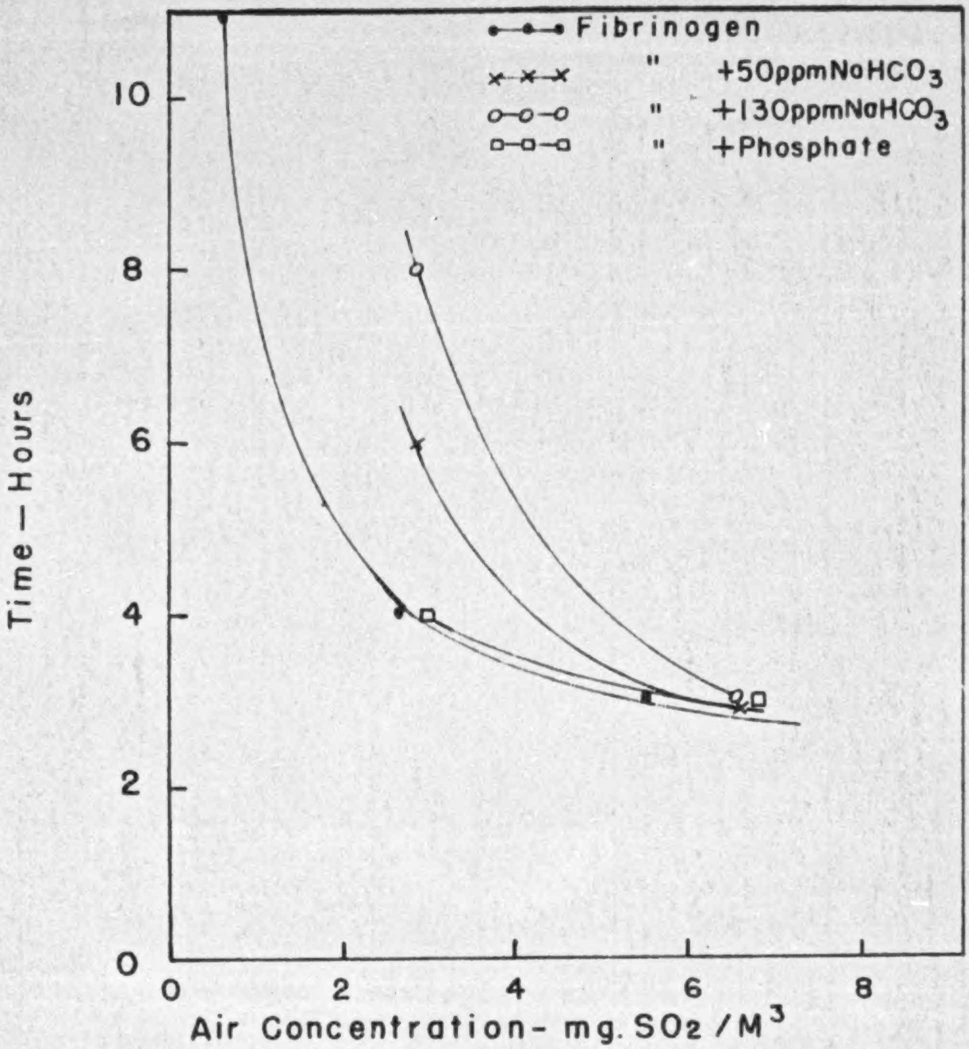

FIGURE 54 - TIME FOR 0.159% FIBRINOGEN SOLUTION TO REACH MAXIMUM TURBIDITY WHEN EXPOSED TO ATMOSPHERIC SULFUR DIOXIDE

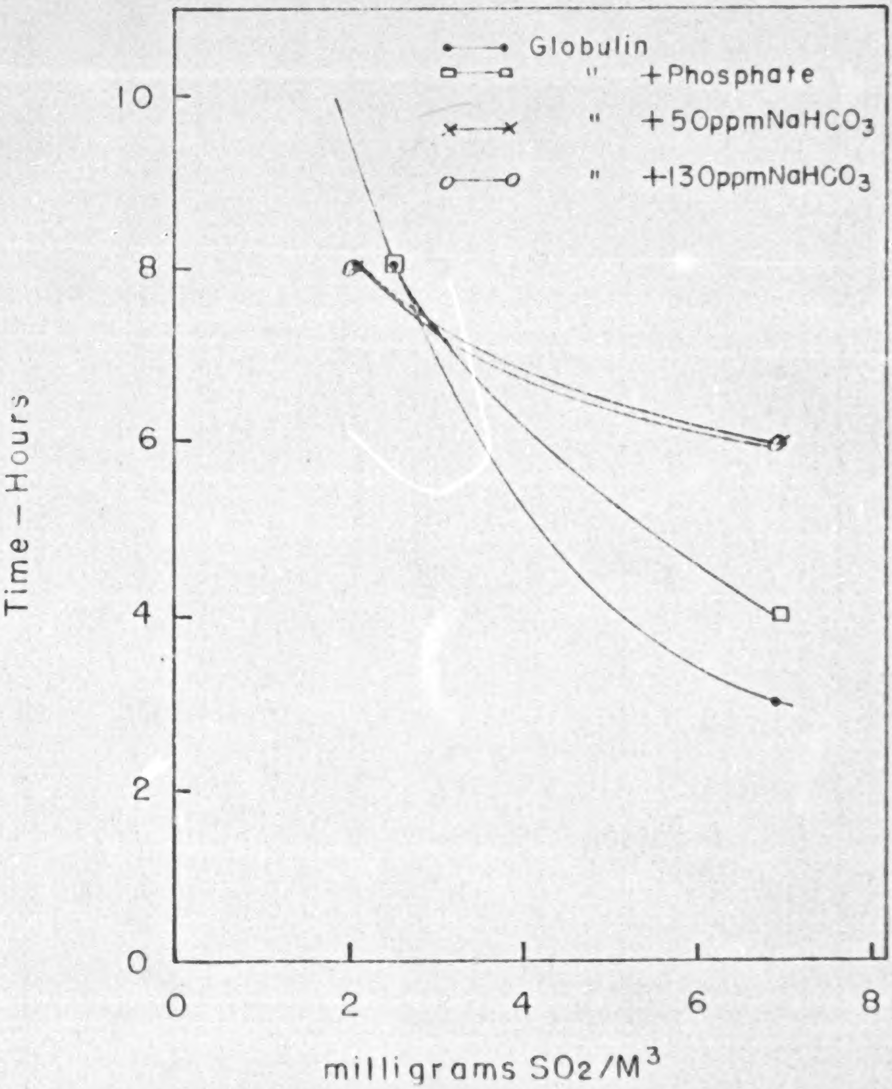

FIGURE 55 - TIME TO START OF COAGULATION OF 0.159% GLOBULIN SOLUTION EXPOSED TO ATMOSPHERIC SULFUR DIOXIDE

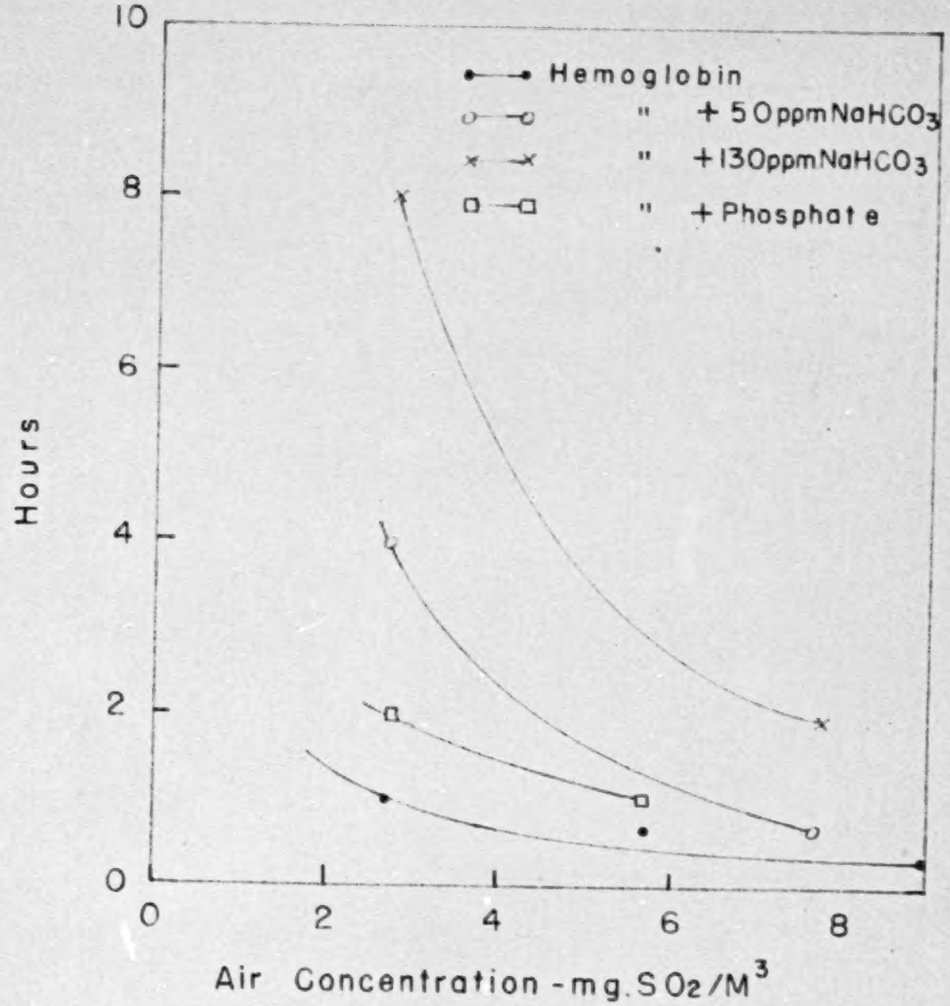

FIGURE 56 - ELAPSED TIME BEFORE START OF TRANSFORMATION OF 0.159% HEMOGLOBIN SOLUTION EXPOSED TO VARIOUS CONCENTRATIONS OF ATMOSPHERIC SULFUR DIOXIDE

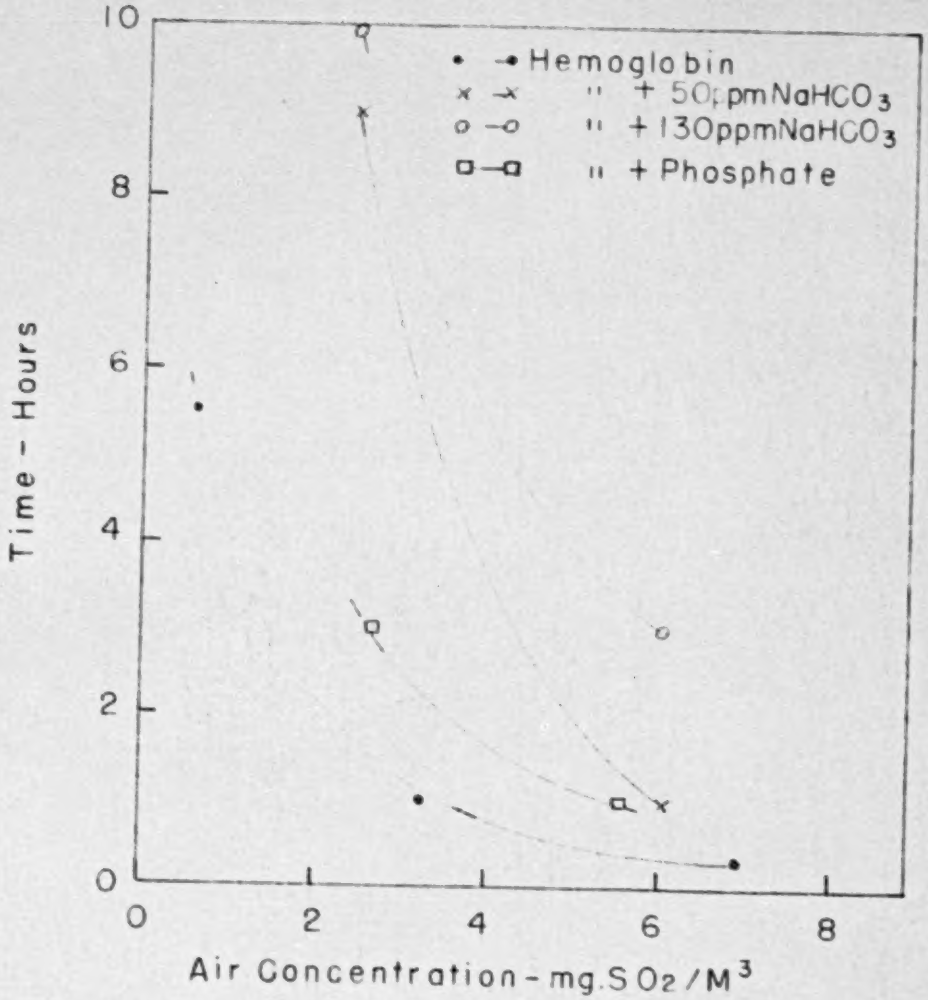

FIGURE 57 - ELAPSED TIME BEFORE START OF TRANSFORMATION OF 50 ppm HEMOGLOBIN SOLUTION EXPOSED TO VARIOUS CONCENTRATIONS OF ATMOSPHERIC SULFUR DIOXIDE

Figure 53 shows the time required for maximum turbidity of 0.159 percent albumin solutions exposed to various atmospheric concentrations of sulfur dioxide. At a concentration of 4.0 mg. $SO_2/M^3$ the plain albumin solution reached maximum turbidity in about 1.8 hours. The addition of 130 ppm. sodium bicarbonate in the albumin solution delayed the maximum turbidity to 6.0 hours.

Figure 54 shows the time required for maximum turbidity of 0.159 percent fibrinogen solutions exposed to several atmospheric concentrations of sulfur dioxide. The fibrinogen solutions reached maximum turbidity in 3.4 hours when exposed to a concentration of 4.0 mg. $SO_2/M^3$. With 130 ppm. of sodium bicarbonate added to the fibrinogen solution the maximum turbidity was delayed to 5.4 hours.

Figure 55 is the time for the start of the coagulation of 0.159 percent globulin solutions. At an atmospheric concentration of 4.0 mg. $SO_2/M^3$ it took 5.3 hours for the coagulation to occur. The addition of 130 ppm. of sodium bicarbonate extended the time to 6.8 hours.

The transformation of the 0.159 percent hemoglobin solution did not start immediately after exposure, but the time varied inversely as the atmospheric concentration, as shown in Figure 56. It can be seen that at higher concentrations of atmospheric sulfur dioxide, the time required before transformation of the hemoglobin was noted was less than at lower atmospheric concentrations. At a concentration of 4.0 mg. $SO_2/M^3$ it took 50 minutes before the 0.159 percent hemoglobin solution reacted. The addition of 130 ppm. of sodium bicarbonate to the protein solution extended the time to over five hours.

Figure 57 is the time for the start of transformation of the 50 ppm. hemoglobin solution exposed to several concentrations of atmospheric sulfur dioxide. The transformation of the hemoglobin started in 50 minutes at an air concentration of 4.0 mg. $SO_2/M^3$ when the plain protein was exposed. When 130 ppm. of sodium bicarbonate were added to the hemoglobin solution the time was extended to 5.8 hours.

d) pH of Exposed Protein Solutions.--The pH of the protein solutions at the time of the reactions with dissolved sulfur dioxide was measured. In the case of the albumin and fibrinogen the relationships shown in Figures 58 to 61 were obtained. It can be seen in Figures 58 and 59 that the maximum turbidity of the albumin solutions, whether buffered or not, occurred at a pH value near 5.0, with slightly higher values when the buffers were present.

In the case of fibrinogen, Figures 60 and 61, it can be seen that no turbidity was noted until the pH reached approximately 5.3, in both the buffered and unbuffered solutions. The maximum turbidity of the fibrinogen solutions occurred at a pH below 5.0 and in the range of 4.6 to 5.0.

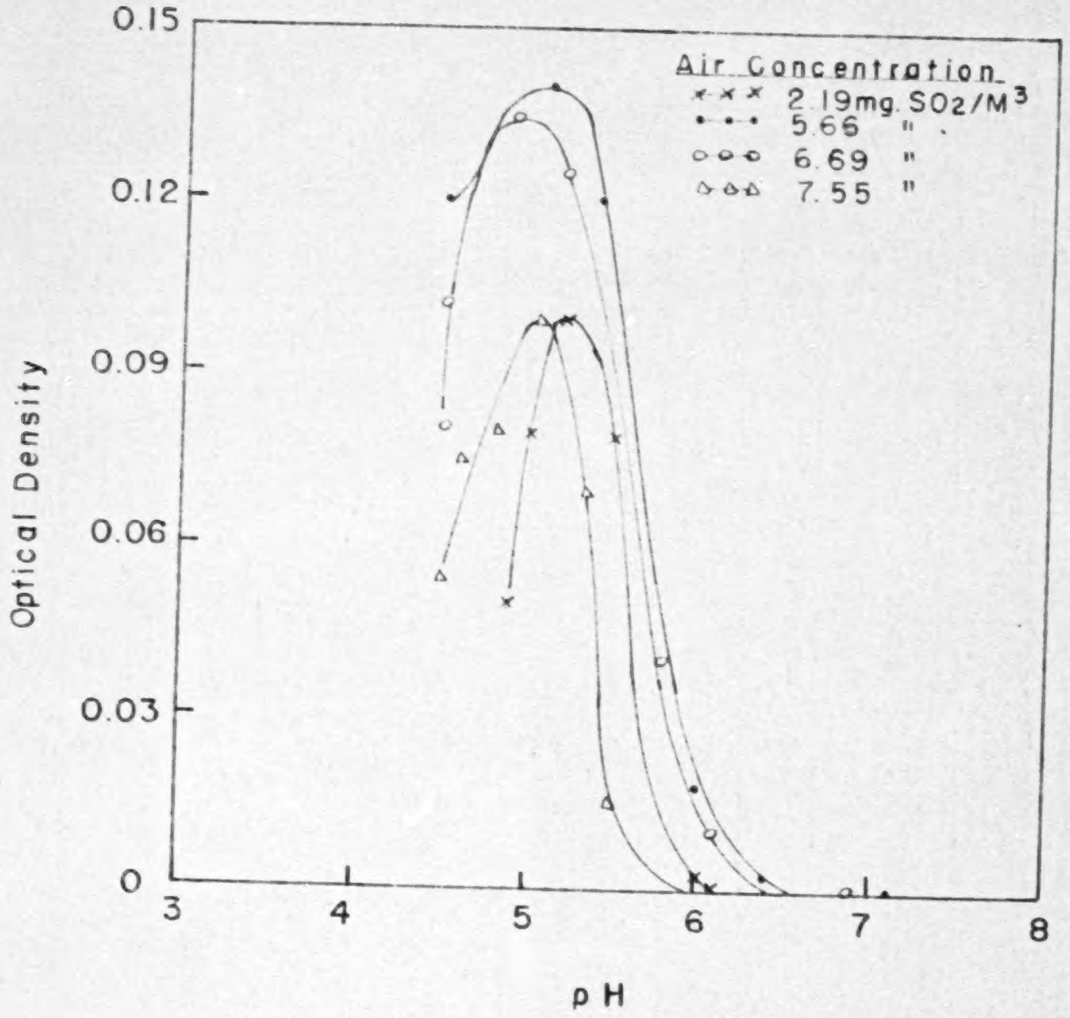

FIGURE 58 - EFFECT OF pH ON TURBIDITY OF 0.159% EGG ALBUMIN SOLUTION EXPOSED TO ATMOSPHERIC SULFUR DIOXIDE

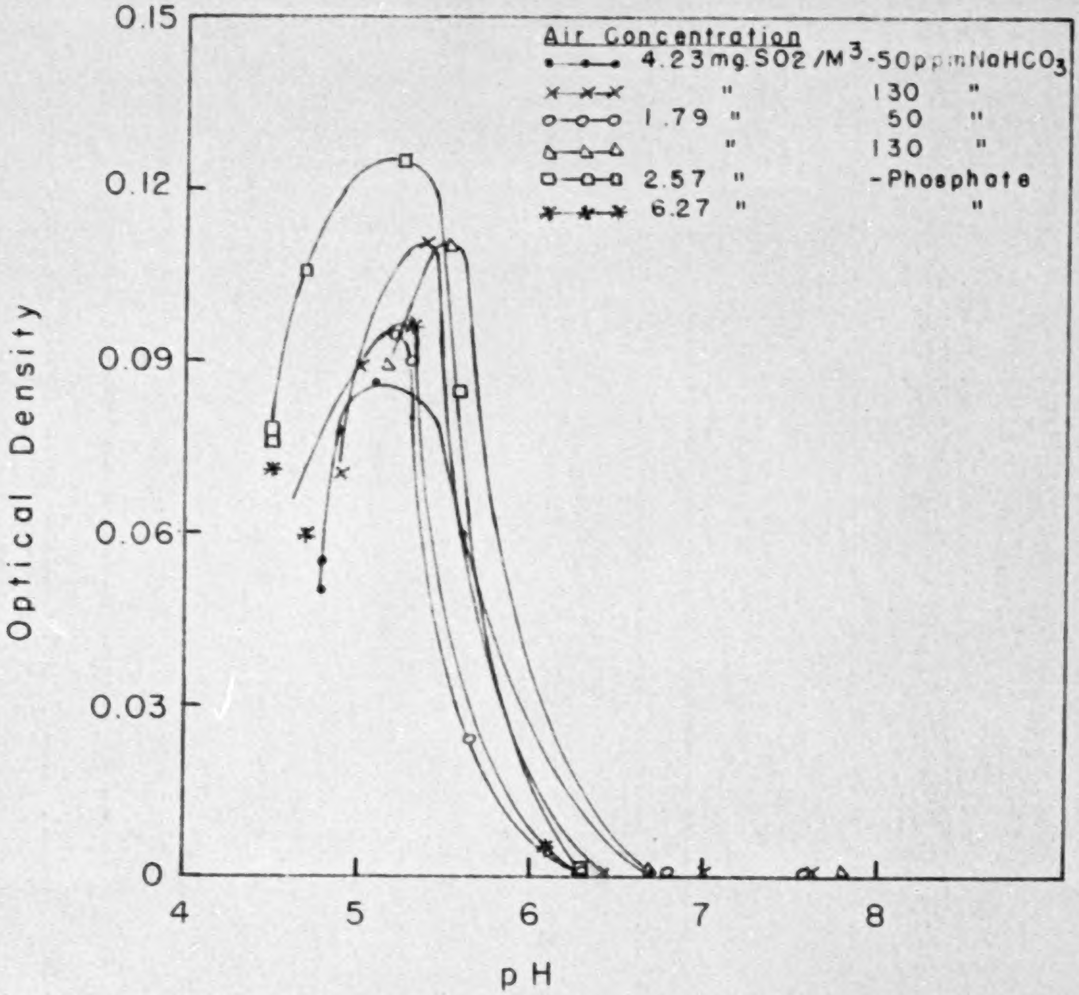

FIGURE 59 - EFFECT OF pH ON TURBIDITY OF BUFFERED 0.159% EGG ALBUMIN SOLUTIONS EXPOSED TO ATMOSPHERIC SULFUR DIOXIDE

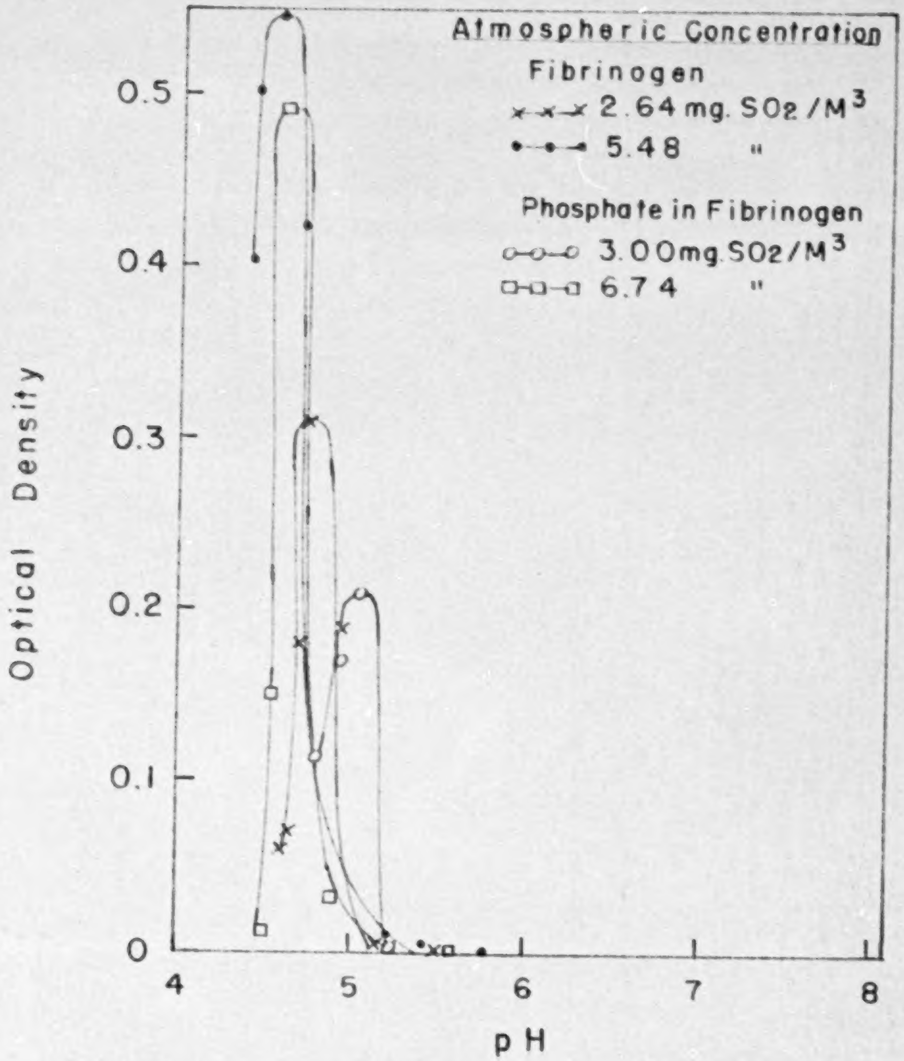

FIGURE 60 - EFFECT OF pH ON TURBIDITY OF A 0.159% FIBRINOGEN IN 3% SODIUM CHLORIDE SOLUTION EXPOSED TO ATMOSPHERIC SULFUR DIOXIDE

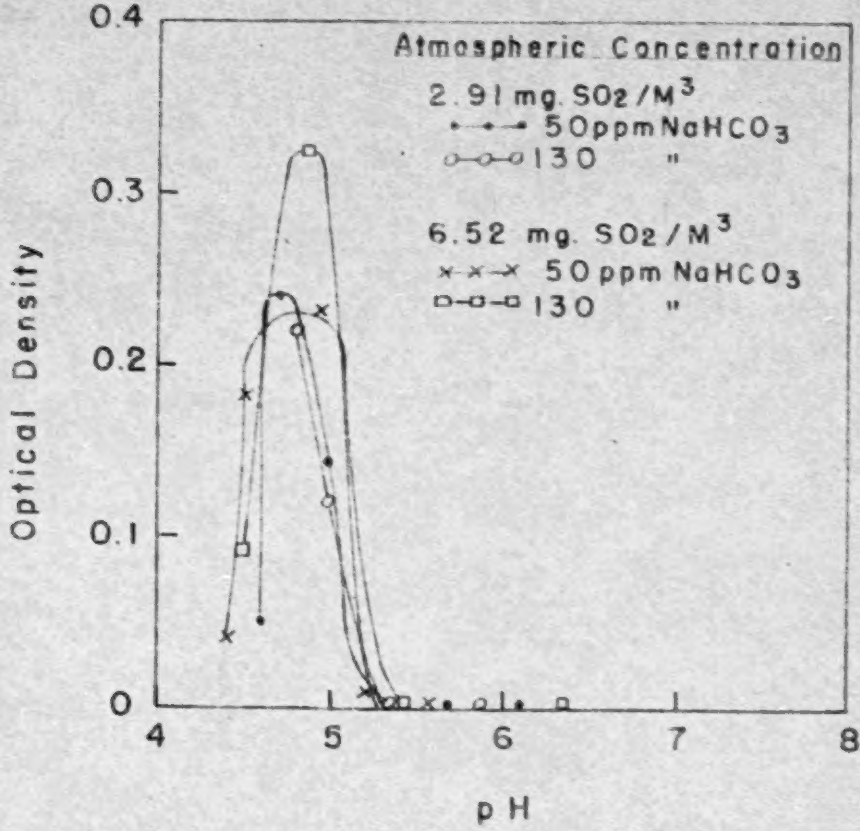

FIGURE 61 - EFFECT OF pH ON TURBIDITY OF BICARBONATE BUFFERED FIBRINOGEN SOLUTIONS EXPOSED TO ATMOSPHERIC SULFUR DIOXIDE

When globulin solutions were exposed no relationship was found between the degree of turbidity and the pH of the solution. It was observed, however, that no coagulation occurred until the pH of the exposed globulin solutions reached 5.5.

In the case of the 0.159 percent hemoglobin solutions, it was noted that no transformation of the protein took place until the pH of the solution had reached a value near 6.0. No correlation was found between further pH changes and the amount of hemoglobin found in solution except that the amount of protein that was transformed increased markedly with only slight decreases in the pH value.

Similar results were obtained with the 50 ppm. hemoglobin solutions with the exception that the transformation of the protein did not occur until the pH reached a value of 5.0. In this case, also, no correlation was found between further pH changes and the amount of hemoglobin found in solution.

e) Titration of Protein Solutions with Sulfuric and Sulfurous Acid.--Samples of buffered and unbuffered protein solutions were titrated with 0.02N sulfuric acid and 0.05N sulfurous acid. The pH of the samples was measured at increment additions of the acid and the protein reaction noted. The results are shown in Figures 62 to 67.

Figures 62 and 63 indicate that the maximum turbidity in the albumin solutions occurred when the pH was below 5.0 when the solutions were titrated with sulfuric and sulfurous acid.

It can be seen from Figures 64 and 65 that the maximum turbidity of the fibrinogen solutions occurred at a pH value below 5.0 and in no case was turbidity noted until the pH reached a value of 5.4.

Figures 66 and 67 show that no turbidity was observed in the globulin solutions until the pH of the solution had decreased to a value near 5.5.

The difference in the magnitude of the turbidity shown in Figures 30 to 35 for the individual proteins was due to dilution. Samples containing sodium bicarbonate required more acid to bring the pH to any particular level, and this served to dilute the sample so that the maximum turbidity appeared to be lower.

In the case of the hemoglobin solutions, it was observed that no transformation occurred in the titrated solutions until the pH reached a value of 6.0 for the 0.159 percent solution and a value of 5.0 for the 50 ppm. hemoglobin solutions.

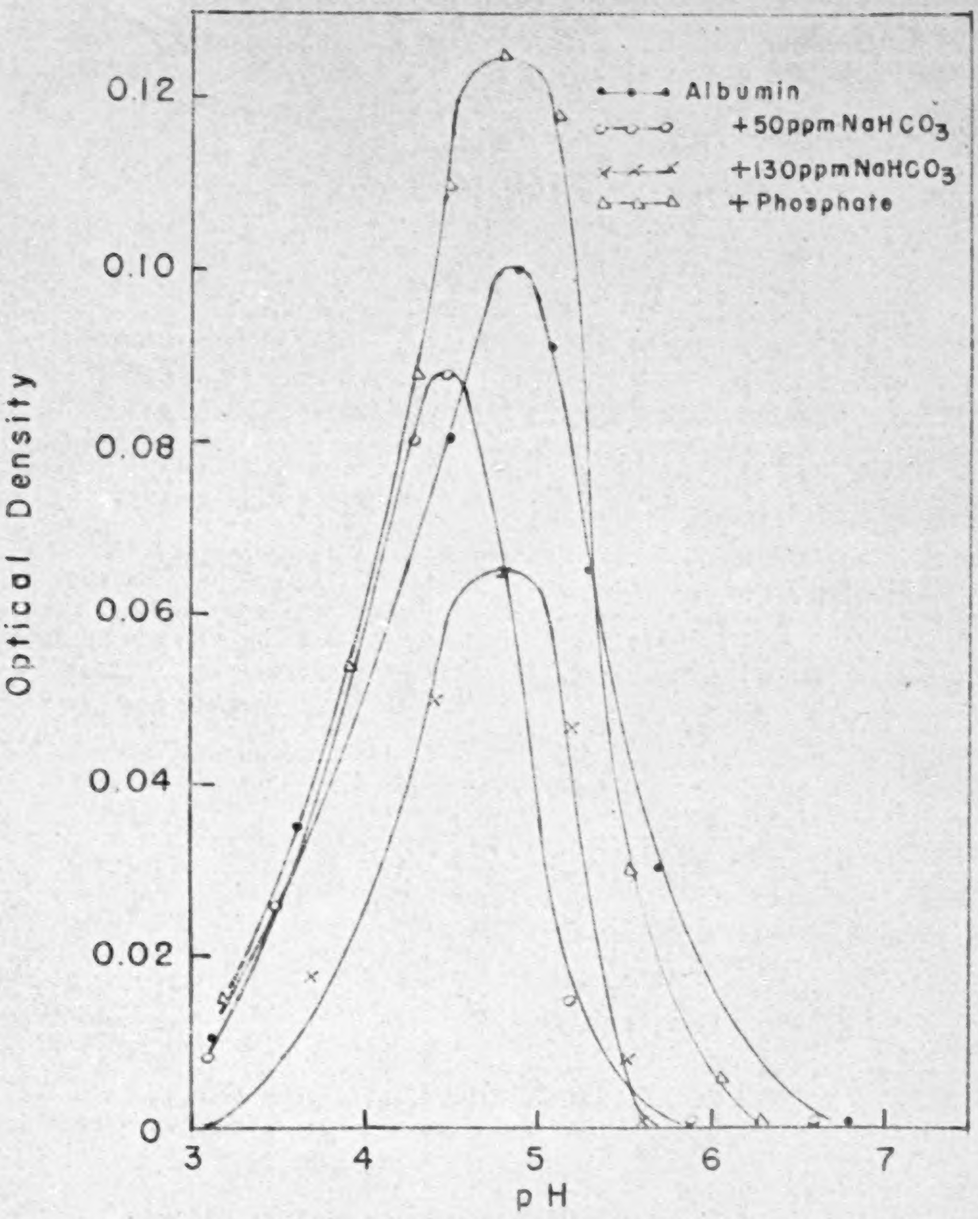

FIGURE 62 - EFFECT OF pH ON TURBIDITY OF 0.159% EGG ALBUMIN SOLUTIONS TITRATED WITH 0.02N $H_2SO_4$

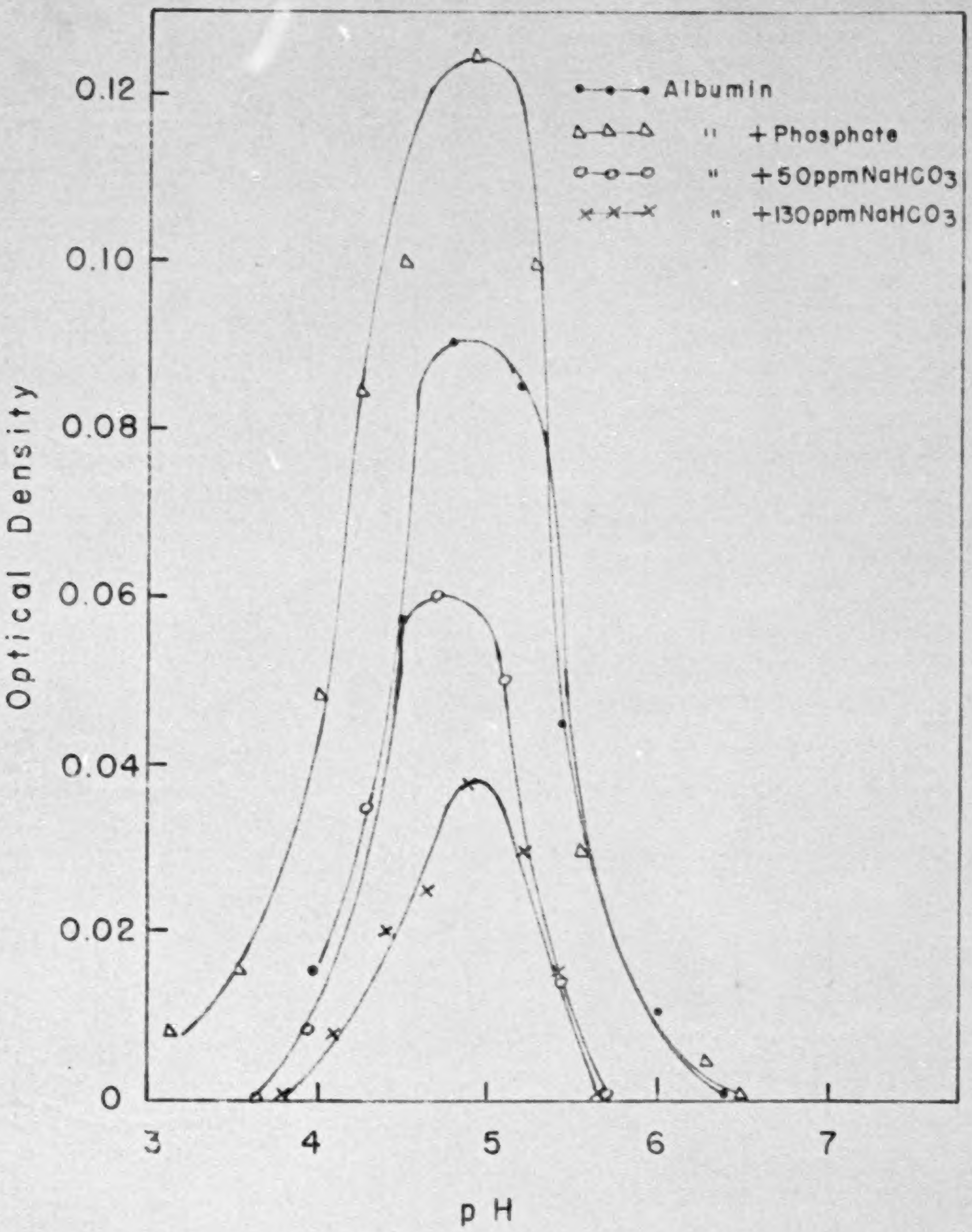

FIGURE 63 - EFFECT OF pH ON TURBIDITY OF 0.159% EGG ALBUMIN SOLUTIONS TITRATED WITH 0.05N $H_2SO_3$

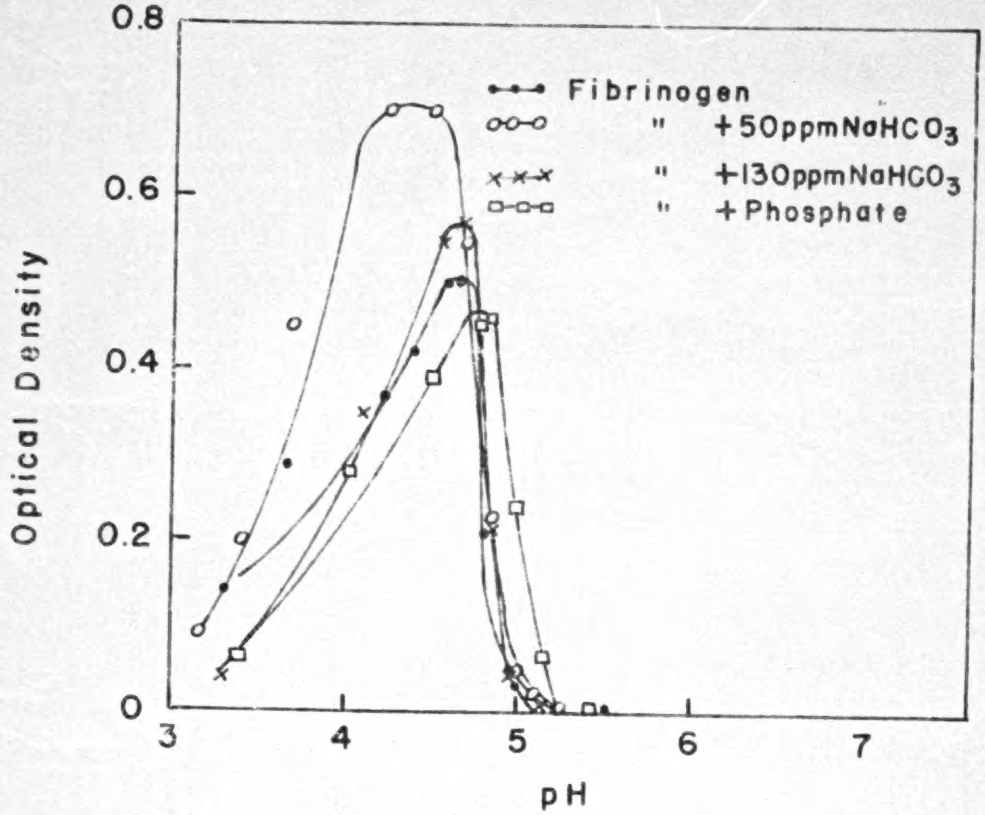

FIGURE 64 - EFFECT OF pH ON TURBIDITY OF 0.159% FIBRINOGEN SOLUTION TITRATED WITH 0.02N $H_2SO_4$

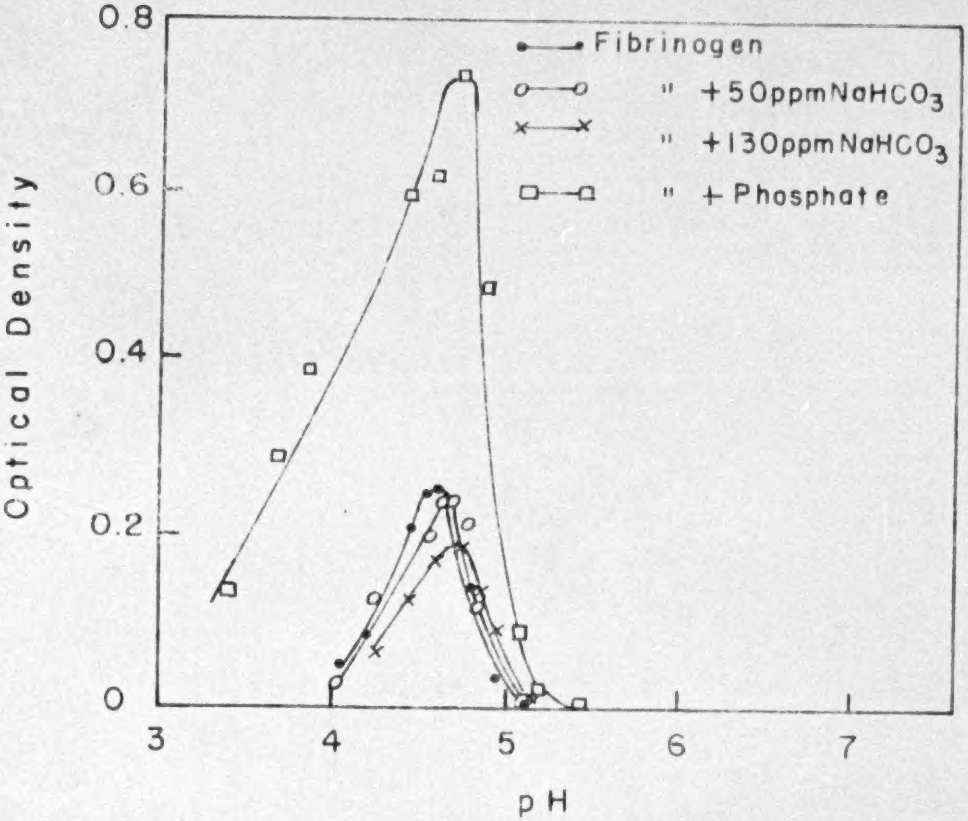

FIGURE 65 - EFFECT OF pH ON TURBIDITY OF 0.159% FIBRINOGEN SOLUTIONS TITRATED WITH 0.05N $H_2SO_3$

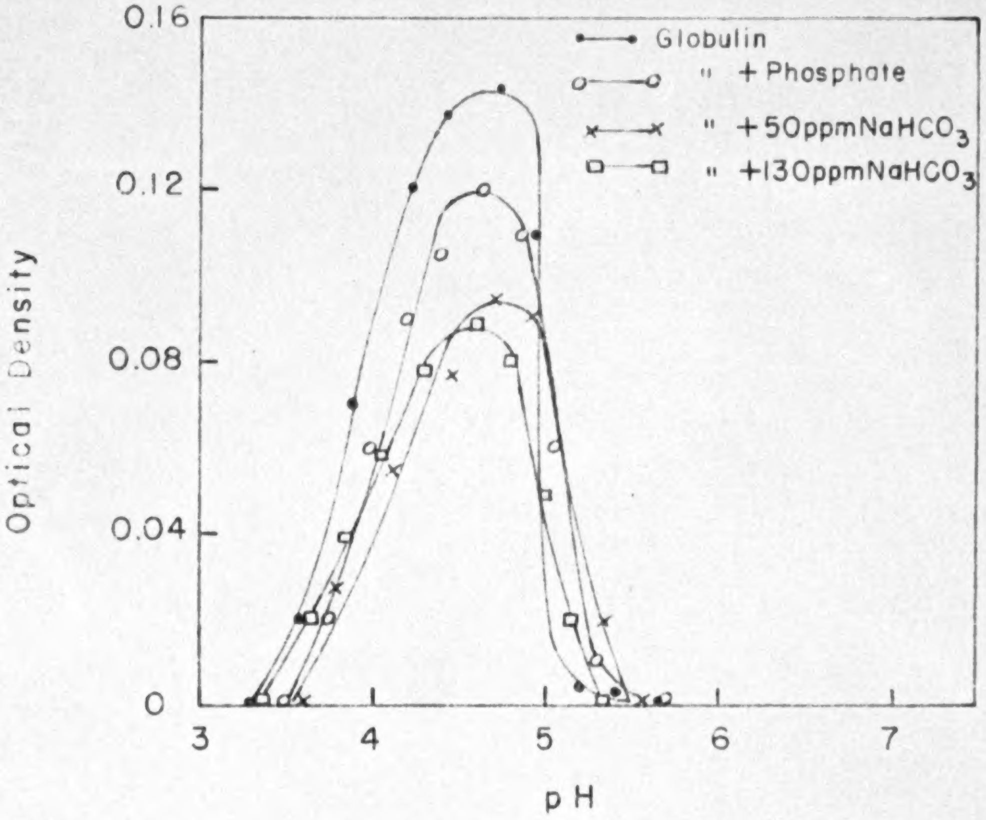

FIGURE 66 - EFFECT OF pH ON TURBIDITY OF 0.159% GLOBULIN SOLUTIONS TITRATED WITH 0.02N $H_2SO_4$

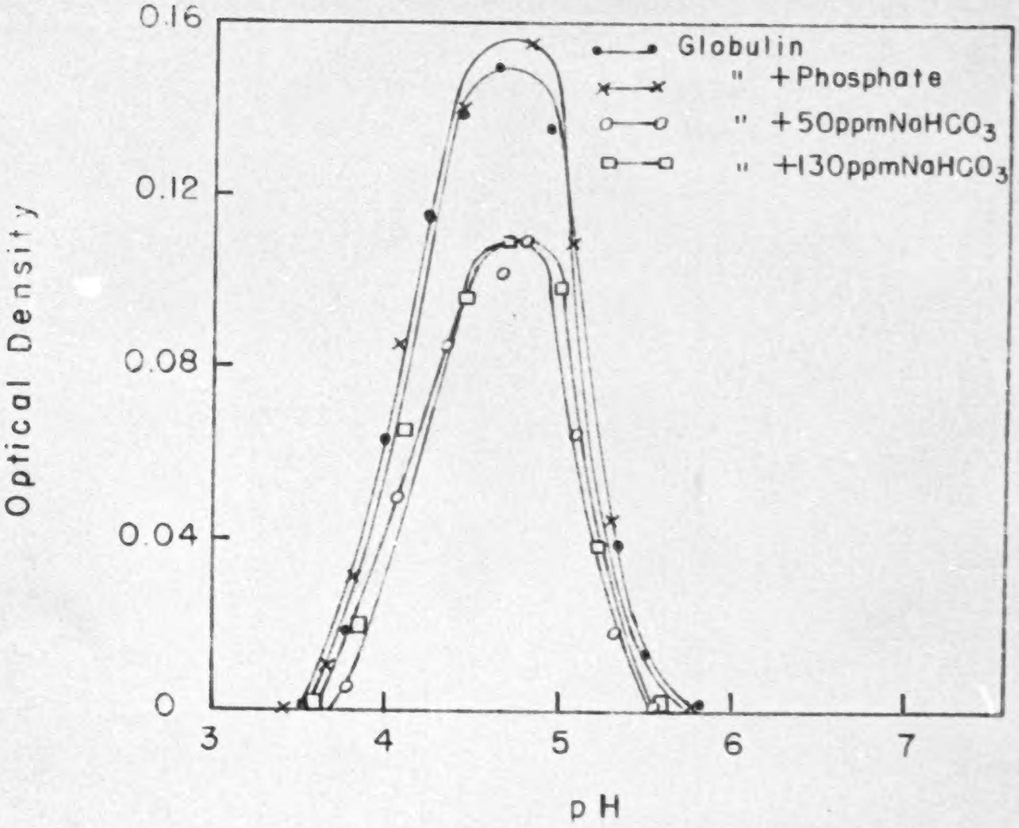

FIGURE 67 - EFFECT OF pH ON TURBIDITY OF 0.159% GLOBULIN SOLUTIONS TITRATED WITH 0.05N $H_2SO_3$

A comparison of the pH of the protein solutions at which reaction took place, both in atmospheric exposures and in the titrated samples, is given for each of the proteins in Tables XXIV to XXVII.

From Table XXIV it can be seen that the maximum turbidity of the albumin solutions occurred when the pH was near 5.0 and the range was 4.5 to 5.4.

The maximum turbidity of the fibrinogen solutions, shown in Table XXV, occurred when the pH was near 4.70 and the range was 4.4 to 5.05.

It can be seen from Table XXVI that the coagulation of the globulin solutions started when the pH is near 5.5 and the range is 5.3 to 5.8.

The pH of the 0.159 percent hemoglobin solutions at the time at which transformation was first noted is given in Table XXVII. It can be seen that no transformation of the hemoglobin took place until the pH of the solution decreased to a value near 6.0. The same effect was noted with the 50 ppm. hemoglobin solution, but the pH at which the transformation was noted was approximately 5.0 for both exposed and titrated samples. The range for the 50 ppm hemoglobin solutions shown in Table XXVII was 4.2 to 5.1.

Based on the data presented, it may be concluded that the reaction of sulfur dioxide and the proteins was due to the hydrogen ions released upon solution of atmospheric sulfur dioxide. Titration with sulfuric acid showed no appreciable differences from the titration with sulfurous acid, and these in turn did not show a significant difference from the protein solutions exposed to the various concentrations of atmospheric sulfur dioxide.

The presence of sodium bicarbonate and phosphate provided a buffer capacity to the protein solution that prevented rapid decreases in the pH value when the protein solutions were exposed to atmospheric sulfur dioxide.

f) Sulfite Recovery in Centrifuged Albumin Samples.--Further analysis of the reaction of sulfur dioxide was carried out by separation of precipitated albumin from the supernatant followed by determination of the sulfite in each fraction. The procedure was to expose several albumin solutions in the test chamber to an atmosphere containing 7.50 mg. $SO_2/M^3$ for one hour. The exposure was of sufficient length to decrease the pH of the solution to a value near 5.0. Centrifugation was used to separate the coagulated protein. Several albumin solutions were treated as follows:

## TABLE XXIV

## pH OF 0.159% ALBUMIN SOLUTIONS AT MAXIMUM TURBIDITY

| Solution | Atmospheric Exposure | Titrated ($H_2SO_4$) | Titrated ($H_2SO_3$) |
|---|---|---|---|
| Albumin alone | 4.90<br>5.05<br>5.10<br>5.20 | 4.90 | 4.80 |
| 50 ppm. $NaHCO_3$ in Albumin | 5.10<br>5.40 | 4.50 | 4.70 |
| 130 ppm. $NaHCO_3$ in Albumin | 5.15<br>5.20 | 4.80 | 4.90 |
| Phosphate in Albumin | 5.25<br>5.30 | 4.80 | 4.95 |

## TABLE XXV

## pH OF 0.159% FIBRINOGEN SOLUTIONS AT MAXIMUM TURBIDITY

| Solution | Atmospheric Exposure | Titrated ($H_2SO_4$) | Titrated ($H_2SO_3$) |
|---|---|---|---|
| Fibrinogen alone | 4.55 | 4.65 | 4.55 |
| 50 ppm. $NaHCO_3$ in Fibrinogen | 4.70<br>4.80 | 4.40 | 4.65 |
| 130 ppm. $NaHCO_3$ in Fibrinogen | 4.80<br>4.85 | 4.60 | 4.75 |
| Phosphate in Fibrinogen | 4.60<br>5.05 | 4.75 | 4.70 |

## TABLE XXVI

## pH OF 0.159% GLOBULIN SOLUTIONS AT THE START OF COAGULATION

| Solution | Atmospheric Exposure | Titrated ($H_2SO_4$) | Titrated ($H_2SO_3$) |
|---|---|---|---|
| Globulin alone | 5.5<br>5.5<br>5.8 | 5.4 | 5.8 |
| 50 ppm. $NaHCO_3$ in Globulin | 5.5<br>5.7 | 5.5 | 5.5 |
| 130 ppm. $NaHCO_3$ in Globulin | 5.3 | 5.3 | 5.6 |
| Phosphate in Globulin | 5.5<br>5.5 | 5.6 | 5.7 |

## TABLE XXVII

## pH OF 0.159% HEMOGLOBIN SOLUTIONS AT WHICH TRANSFORMATION OCCURRED

| Solution | Atmospheric Exposure | Titrated ($H_2SO_4$) | Titrated ($H_2SO_3$) |
|---|---|---|---|
| Hemoglobin alone | 5.35<br>5.80<br>5.80 | 5.40 | 5.80 |
| 50 ppm. $NaHCO_3$ in Hemoglobin | 5.90<br>6.10 | 5.90 | 5.80 |
| 130 ppm. $NaHCO_3$ in Hemoglobin | 5.90<br>6.30 | 5.90 | 6.10 |
| Phosphate in Hemoglobin | 5.00<br>5.60 | 5.80 | 6.10 |

### TABLE XXVIII

### pH OF 50 ppm. HEMOGLOBIN SOLUTIONS AT WHICH TRANSFORMATIONS TOOK PLACE

| Solution | Atmospheric Exposure | Titrated ($H_2SO_4$) | Titrated ($H_2SO_3$) |
|---|---|---|---|
| Hemoglobin | 4.20<br>4.25<br>4.30 | 4.90 | 4.20 |
| 50 ppm. $NaHCO_3$ in Hemoglobin | 4.60<br>4.85 | 4.60 | 4.50 |
| 130 ppm. $NaHCO_3$ in Hemoglobin | 4.90<br>5.10 | 4.50 | 5.20 |
| Phosphate in Hemoglobin | 4.40<br>4.45 | 4.90 | 5.10 |

| Sample | Treatment |
|---|---|
| A | Exposed to atmospheric sulfur dioxide. |
| B | Supernatant of a sample after exposure to atmospheric sulfur dioxide. |
| C | Precipitate of a sample after exposure to atmospheric sulfur dioxide. |
| D | Exposed to atmospheric sulfur dioxide for one hour and then deaerated with nitrogen. |
| E | pH adjusted to 5.15 with hydrochloric acid. |
| F | Precipitate of a sample after treatment with hydrochloric acid. |
| G | Supernatant of a sample after treatment with hydrochloric acid. |

The amount of sulfite in each of these samples was determined and the results are presented in Table XXIX.

It can be seen from Table XXIX that the original albumin solution (Sample A) had dissolved 73.73 micrograms $SO_2$/ ml. during the exposure. Separation of the supernatant and precipitate indicated no sulfite was present in the precipitate (Sample C), while the supernatant (Sample B) contained 74.24 micrograms $SO_2$/ ml. Sample D, which was deaerated with nitrogen contained 74.06 micrograms $SO_2$/ ml. which compared favorably with the 73.76 micrograms $SO_2$/ ml. found in the albumin solution exposed for one hour. No sulfite was found in the solutions and precipitate of the samples treated with hydrochloric acid (Samples E, F, and G).

It may be concluded that the coagulation of the protein solutions exposed to atmospheric sulfur dioxide was due to the hydrogen ions released upon solution of the gas.

g. Labelled Sulfur Dioxide.--A sulfurous acid solution was prepared by dissolving $S^{35}O_2$ in distilled water. Sufficient acid was added to 0.159 percent solutions of albumin, fibrinogen, and globulin to bring the pH down to 4.9. The three proteins coagulated at this pH as had been shown previously. The coagulated protein was allowed to stand for a time in order to allow the fine particles to agglomerate and settle. The coagulated protein was filtered through a millipore filter and washed. The wash solution was distilled water in the case of the albumin, and 0.07 percent sodium chloride for the fibrinogen and globulin.

## TABLE XXIX

## SULFITE RECOVERY IN CENTRIFUGED ALBUMIN SAMPLES COAGULATED BY ATMOSPHERIC SULFUR DIOXIDE AND BY HYDROCHLORIC ACID

| Sample | pH | Micrograms $SO_2$/ ml. |
|---|---|---|
| A | 5.05 | 73.76 |
| B | - | 74.24 |
| C | - | 0 |
| D | 5.10 | 74.56 |
| E | 5.15 | 0 |
| F | - | 0 |
| G | - | 0 |

Several pellets of sodium hydroxide were placed in the vacuum flask before the filtration. This prevented volatilization of the $S^{35}O_2$ from the acidified protein solution.

Portions of the filtrate and the millipore filter were dried in an oven on planchets and counted in a gas flow proportional counter. The total counts computed from suitable aliquots are presented in Table XXX.

It was found that between 0.1 and 0.2 percent of the activity added to the original solutions remained on the filter, the rest passing through with the filtrate. From the small amount of $S^{35}$ found on the filter, it may be concluded that, if there is a direct reaction between sulfur dioxide and the three proteins, it is not of very great magnitude. The coagulation of the protein must be due to the decrease in the pH value caused by solution of sulfur dioxide and not to a direct chemical reaction between the dissolved gas and the proteins.

### 4. Discussion.

The exposure of albumin, fibrinogen, globulin, and hemoglobin solutions to atmospheric sulfur dioxide resulted in a solution of the gas in the protein solutions. A comparison of the amount of sulfur dioxide found in the protein solutions exposed to 2.70 mg. $SO_2/M^3$ for four hours is given in Table XXXI. It can be seen that fibrinogen dissolved 59.5 micrograms $SO_2$/ ml., while the hemoglobin solutions contained only 28.0 micrograms/ ml. with the other two proteins having solubilities between these two extremes.

It was found that sodium bicarbonate and phosphates added to the proteins increased the solubility of the atmospheric sulfur dioxide in the solutions. The greater the amount of the buffer, the greater the amount of dissolved sulfur dioxide.

Albumin, fibrinogen, and globulin coagulated when exposed to atmospheric sulfur dioxide. The albumin reached maximum turbidity at is isoelectric point which is a pH of about 4.8. The fibrinogen and globulin started to coagulate when the pH of the solution reached their isoelectric points which are 5.4 for fibrinogen and 5.1 for globulin. The buffered solutions showed the same response at the same pH. If a chemical reaction between sulfur dioxide and the proteins had taken place, then the reaction in the bicarbonate solutions should have been the most extreme since they contained the greatest amount of dissolved sulfur dioxide. Titration with sulfuric acid caused the same type of denaturation at the same pH as occurred in the samples exposed to atmospheric sulfur dioxide. The use of $S^{35}$ showed that less than 0.2 percent of the activity was associated with the precipitated protein, the rest of the activity was associated with the supernatant so that if any reaction occurred between the sulfur dioxide and the protein it had to be of a low order of magnitude.

## TABLE XXX

## COUNTS OBTAINED ON VARIOUS FRACTIONS OF PROTEINS COAGULATED WITH $S^{35}O_2$

| Treatment | Albumin ($10^6$ counts/ min. | Fibrinogen ($10^6$ counts/ min.) | Globulin ($10^6$ counts/ min.) |
|---|---|---|---|
| ml. $S^{35}O_2$ solution added | 16 | 30 | 20 |
| Total activity added | 114.85 | 215.36 | 143.57 |
| Recovered in filtrate | 111.81 | 193.63 | 124.30 |
| Recovered on filter | 0.13 | 0.28 | 0.27 |
| Percent retained (filter/filtrate) | 0.12 | 0.15 | 0.21 |

## TABLE XXXI

## COMPARISON OF THE SOLUBILITY OF ATMOSPHERIC SULFUR DIOXIDE IN 0.159 PERCENT PROTEIN SOLUTIONS EXPOSED FOUR HOURS TO A CONCENTRATION OF 2.70 mg.$SO_2$/$M^3$

| Solution | Micrograms $SO_2$/ml. |
|---|---|
| Distilled water | 8.7 |
| Albumin | 44.2 |
| Fibrinogen | 59.5 |
| Globulin | 38.3 |
| Hemoglobin | 28.0 |

The buffers added to the protein solutions in all cases delayed the reaction of the protein for any specific air concentration which indicated that the reaction was one of a particular pH and not related directly to the amount of sulfur dioxide in solution.

A transformation of hemoglobin occurred when the pH of the solution decreased below 6.0 as evidenced by a decrease in absorbance at a wavelength of 625 millimicrons. This again was not a reaction that was specific for sulfur dioxide but rather one of acidity of the solutions of the gas. The same type of reaction was brought about by titration of the sample with sulfuric acid.

## GENERAL DISCUSSION

A laboratory study was conducted to determine the rate and extent of absorption of atmospheric sulfur dioxide by water surfaces. The information was gathered to aid in the assessment of damage to materials by solutions of acid gases, to provide information for determination of possible health effects, and to determine the possible role of various surfaces on the removal of sulfur dioxide from the atmosphere.

The rate of solution of atmospheric sulfur dioxide in distilled water films was found to be a function of the concentration of sulfur dioxide in the atmosphere. The higher the concentration in the air, the more rapidly the solution reached a saturation value. It was found that over the range of atmospheric concentrations of 0.81 to 8.73 mg. $SO_2/M^3$ distilled water samples reached saturation in less than 2 hours. Even during the 2-hour period of exposure, the rate of solution during the first portion was more rapid than in the later portions of the exposure period.

These findings indicate that removal of atmospheric sulfur dioxide by rain water is very effective as far as the rate of solution of the gas is concerned. The rain water passes through the air which contains the gas and removes the sulfur dioxide by solution of the gas. By exposing new water surfaces continually, the rate of absorption of the gas into the water remains at a relatively high level.

In addition to the above, the findings indicated that surface films of water are essentially saturated in 2 hours so that long-term exposure to the same atmospheric concentration of sulfur dioxide would not result in further removals of the gas from the air. Thus a film of water covering non-viable objects would absorb a fixed amount of gas and no further sulfur dioxide would be removed unless the gas in solution reacted with materials dissolved from the supporting objects.

The pH of distilled water samples exposed in the test chamber decreased very rapidly and reached values of 4.0 or less and remained at that level for the period of the exposure. These findings can be compared to the report by Copson (16) who found the pH of fog and cloud water at Bayonne, New Jersey, to be as low as 4.5, and to the findings of Houghton (39) who reported the pH of fog and cloud water occasionally dropped to a value of 3.0 but most often was near 4.0. Both of these investigators credit the solution of acid gases emitted by industrial operations as the cause for the low pH values. Bienstock et al. (8) discussed the solution of acid gases and stated that as an acid gas, such as sulfur dioxide, dissolves the gas is in equilibrium with the ions formed. Thus $H^+ \cdot SO_3^= = k \cdot P_{SO_2}$, and the capacity of a liquid to dissolve sulfur dioxide at any gas concentration is inversely proportional to the hydrogen ion concentration. The rapid rise in hydrogen ion concentration of the distilled water samples is evidenced by the rapid decrease in the pH and the final result was that solution of the gas soon stopped.

The solubility of sulfur dioxide in distilled water did not follow the law of partial pressure. Computation of the amount of un-ionized sulfurous acid in the solution showed that the solubility of this fraction of the dissolved sulfite did follow the law of partial pressures. The value for the constant determined for the solubility of the un-ionized portion of the sulfurous acid was approximately 0.028 micrograms $SO_2$/ml./mg. $SO_2/M^3$. It was possible to calculate the amount of bisulfite and un-ionized sulfurous acid that existed in the water solutions by means of this constant. It was found that over 98.5 percent of the sulfite in solution was in the form of the bisulfite ion. This can be compared to the value reported by Falk and Giguère (24) of only 10 percent of the sulfite in a 1 M. sulfurous acid solution being ionized. Thus it can be seen that in the dilute solutions tested the sulfur dioxide exists predominantly as the bisulfite ion.

The pH of the distilled water solutions that had been exposed to atmospheric sulfur dioxide was shown to have been dependent on the hydrogen ion released upon ionization of the sulfurous acid.

It was found that the overall solubility of sulfur dioxide, both ionized and un-ionized, could be described by an exponential equation of the general type:

$$S = KC^a$$

where "S" is the solubility of atmospheric sulfur dioxide in micrograms/ ml., "C" is the atmospheric concentration of sulfur dioxide in mg./$M^3$ and "a" and "K" are constants that describe the rate and intercept on a log plot of the exponential equation.

Different values for "a" and "K" were obtained for all of the water solutions tested. With these constants it was possible to predict the solubility of atmospheric sulfur dioxide in any of the water solutions tested over the range of 0.5 to 10.0 mg. $SO_2/M^3$.

The addition of phosphate and bicarbonate buffers to distilled water solutions increased the amount of sulfur dioxide dissolved by the solution when it was exposed to atmospheric concentrations of the gas. The phosphate in the solution reacted with the sulfur dioxide and the pH of the resultant solution was due to the gas that was dissolved in excess of that which reacted with the phosphate.

A check of the recovered sulfur dioxide found in the sodium bicarbonate solutions exposed to atmospheres of the gas showed that there was less sulfur dioxide in solution than could be accounted for by reaction with all of the bicarbonate. A similar discrepancy was noted in the sodium bicarbonate solutions that contained sodium chloride, but in this case there was the additional result of a minimum or lag in the recovered sulfur dioxide in the solutions. Exposed sea water samples showed the same pattern in the recovered sulfur dioxide.

In the bicarbonate solutions there is always the possibility of loss of carbon dioxide from the solution upon acidification of the sample. It is possible that an evolution of carbon dioxide took place that changed the partial pressure of the gases over the surface of the exposed liquid. This would have the effect of changing the rate and extent of solution of the gas. Another mechanism that possibly occurred was mechanical scrubbing of gas from the solution by evolution of carbon dioxide and the removal of some of the dissolved sulfur dioxide leading to apparent low recoveries of the gas in solution.

When fibrinogen samples were prepared, a three percent sodium chloride solution was the solvent. To some of the samples of fibrinogen sodium bicarbonate was added before the samples were exposed. In this case no lag or minimum was noted as found when sodium bicarbonate-sodium chloride solutions were exposed. Even in this case the increase in the amount of sulfur dioxide found in the exposed fibrinogen solutions was not equal to the amount of bicarbonate added.

The results presented here did not suggest any definite reaction that was taking place in solutions containing sodium bicarbonate, but it was noted that the systems that did not follow the expected patterns of solution all contained sodium bicarbonate. The possibility of evolution of carbon dioxide upon acidification of the samples was present in all cases, but its effect on the solution of atmospheric sulfur dioxide was not determined in these studies.

Two types of New Jersey soil were tested for their adsorption capacities for sulfur dioxide. In the near-dry state, Lakewood soil, with a pH near 4.0, did not adsorb any atmospheric sulfur dioxide. It was found that a Freundlich equation could be used to describe the adsorption of atmospheric sulfur dioxide by the Nixon type soil. By means of this equation it was possible to calculate the adsorption of sulfur dioxide at any atmospheric concentration.

Soil moisture was found to have a significant influence on the amount of atmospheric sulfur dioxide taken up by a soil sample. Even very acid soil, such as the Lakewood type, adsorbed significant amounts of sulfur dioxide when moisture was present. While the pH of a soil had a marked influence on the amount of sulfur dioxide that was removed by the soil, the moisture content of the soil can greatly increase the amount of sulfur dioxide that is retained.

It was found that the presence of the soil greatly increased the amount of sulfur dioxide taken up by the moisture. From the studies on the water systems alone it had been determined that the amount of sulfur dioxide absorbed by a volume of water reached a particular level and remained at that level with continued exposure of the solution unless something else in the solution reacted with the dissolved sulfur dioxide. The results from the exposure of moistened soil samples indicated many fold increases in the solubility of the gas in water in contact with the soils. This would indicate a reaction of sulfur dioxide with some of the soluble components of the soil.

Exposure of 0.159 percent solutions of albumin fibrinogen, globulin, and hemoglobin to atmospheric sulfur dioxide showed that the solubility of the gas followed the same pattern as that exhibited by distilled water. In the case of the proteins, however, more sulfur dioxide was dissolved at any one atmospheric concentration than was dissolved by distilled water. This was due to the buffer capacity of solutions of the proteins which assisted in maintaining a higher pH for a longer period of time so that more sulfur dioxide would dissolve.

Albumin, fibrinogen, and globulin coagulated near their isoelectric points. The addition of phosphate and bicarbonate buffers delayed the coagulation at any particular atmospheric concentration, but once the pH value decreased, the coagulation took place.

The transformation of the hemoglobin that took place was not a reaction that was specific for sulfur dioxide, but rather one of acidity of solutions of the gas.

## SUMMARY

A laboratory study was conducted to determine the rate and extent of absorption of atmospheric sulfur dioxide by thin films of water solutions. In addition, the adsorption of atmospheric sulfur dioxide by two types of New Jersey soils was measured and the influence of soil moisture was determined.

Exposure of twenty ml. portions of the test solutions was carried out in an environmental chamber in which concentrations of atmospheric sulfur dioxide ranging from 0.5 to 10 mg./$M^3$ could be maintained. The samples were exposed for various periods of time up to eight hours.

It was found that the solubility of atmospheric sulfur dioxide in the water solutions could be described by an exponential equation with the general form $S = KC^a$. The constants were determined and the solubility in four hours was computed for an atmospheric concentration of 2.70 mg. $SO_2/M^3$. For distilled water the value was 8.7 micrograms/ ml. When 50 ppm. of sodium bicarbonate was added to the water, the solubility increased to 32.0 micrograms/ ml., and with 130 ppm. of sodium bicarbonate the solubility increased further to 40.8 micrograms/ ml.

It was found that over 98.5 percent of the sulfur dioxide in the dilute solutions tested existed as the bisulfite and the rest was present as un-ionizedsulfurous acid. While the overall solubility of atmospheric sulfur dioxide did not follow the law of partial pressures, the solubility of the un-ionized portion was found to follow the partial pressure. The Henry's law constant was determined to be 0.0265 micrograms/ ml. /mg. $SO_2/M^3$.

Four proteins; albumin, fibrinogen, globulin, and hemoglobin, were prepared in distilled water at concentrations of 0.159 percent and exposed in the same manner as the plain distilled water samples. It was found that albumin, fibrinogen, and globulin coagulated at their isoelectric points. Bicarbonates and phosphates delayed the coagulation, but once the pH decreased to the isoelectric values, the denaturation took place. For albumin the coagulation occurred at a pH of 4.8; for fibrinogen the coagulation occurred when the pH reached 5.4; and globulin coagulated at a pH value of 5.0.

The use of $S^{35}O_2$ indicated that only 0.1 to 0.2 percent of the activity was associated with the precipitated protein.

Transformation of hemoglobin occurred as evidenced by a decrease in the absorbance of a solution read at 625 millimicrons.

All of the reactions noted in the protein solutions exposed to atmospheric sulfur dioxide were duplicated by titration with sulfuric acid and did not represent specific chemical reactions of sulfur dioxide with the proteins.

Near dry Nixon soil was found to retain 1,134 micrograms of sulfur dioxide when 600 liters of air containing 6.03 mg. $SO_2/M^3$ was passed through 10 grams of the soil. Two percent soil moisture increased the retention to 1,908 micrograms; 5 percent to 2,885; and 10 percent to 2,909 micrograms.

Near dry Lakewood soil was found to retain no sulfur dioxide when 600 liters of air containing 7.27 mg. $SO_2/M^3$ was passed through 25 grams of the soil. When 2 percent moisture was present 285 micrograms of sulfur dioxide was retained, and this increased to 383 micrograms at 5 percent moisture, and to 567 micrograms with 10 percent moisture.

# CONCLUSIONS

The conclusions drawn from this study are:

1. The solubility of the un-ionized portion of sulfur dioxide in solution follows the law of partial pressure.

2. In sulfur dioxide solutions of approximately $0.2 \times 10^{-4}$M over 98 percent of the sulfite in solution is in the form of bisulfite. The rest is essentially in the un-ionized form.

3. The overall solubility of atmospheric sulfur dioxide in distilled water solutions after four hours exposure over the concentration range of 0.5 to 10.0 mg. $SO_2/M^3$ can be described by an exponential equation of the general form $S = KC^a$; where "S" is the solubility in micrograms/ ml. and "C" is the atmospheric concentration in mg./$M^3$.

4. Phosphate and sodium bicarbonate addition to water and protein solutions increase the solubility of atmospheric sulfur dioxide by providing a buffer capacity that prevents rapid decrease in the pH value and allows more sulfur dioxide to dissolve.

5. Within the time limits of exposure used in this study, 8 hours, the solution of sulfur dioxide in water essentially ceases when the pH of the solution reaches 4.0.

6. Dry acid soils do not remove sulfur dioxide from the air, but more alkaline soils can retain significant quantities of the gas.

7. Moisture in soil increases the amount of sulfur dioxide that will be retained by a soil so that all soils can be said to remove sulfur dioxide. The exact amount depending on the pH of the soil and its water content.

8. Natural sea water will dissolve twice as much atmospheric sulfur dioxide as distilled water.

9. Coagulation of albumin, fibrinogen, and globulin exposed to atmospheric sulfur dioxide is due primarily to the releases of hydrogen ion caused by solution of the gas.

10. Bicarbonate and phosphate buffers added to protein solutions increase the time required before a particular concentration of atmospheric sulfur dioxide will cause a denaturation of the protein.

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